# Joint Technical Report

## Validation/Demonstration of Anti-Corrosion Inhibitor Primer Formulations as Replacements for Hexavalent Chromium (Cr(VI)) Military Primer Coatings

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**NAWCWD (Code 4L4200D)**
**1900 N. Knox Road (Stop 6303)**
**China Lake, CA 93555-6106**


**Lead Principal Investigator**
**Dr. Peter Zarras**
**(P) 760-939-1396**
**(F) 760-939-1617**
**Peter.zarras@navy.mil**

**Co-Principle Investigator**
**Ms. Cindy Webber**
**(P) 760-939-2060**
**(F) 760-939-1617**
**Cynthia.webber@navy.mil**


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**14. ABSTRACT** Crosslink has developed a Cr(VI)-free epoxy primer using corrosion-inhibiting compounds (2,5-dimercapto-1,3,4-thiadiazole, DMcT) that have been demonstrated to mimic the corrosion inhibiting properties of Cr(VI). A two-year Environmental Security Technology Certification Program (ESTCP) (WP-200904) FY10-11 was undertaken to prove the viability of this new compound. The tests were performed to access the non-chromium Crosslink coating compatibility with alternative pretreatment coatings and topcoats. Each service, WPAFB, ARL and NAWCWD/NAWCAD and Crosslink tested BAM-PPV, trivalent chromium pretreatment (TCP), CCC and Prekote pretreatments with and without topcoats and the non-chromate Crosslink inhibitor formulations. Each service conducted specific laboratory tests to evaluate the Crosslink primer performance with various pretreatments and in full military coatings (topcoat). Chromated coatings were used as the controls for all accelerated weathering tests. The overall recommendation of the Crosslink primer in its various formulations by each of the services has been that the primer performs best with a chromate pretreatment coating, specifically CCC. Alternative pretreatments such as BAM-PPV, Prekote and TCP do not work with the Crosslink primer system as formulated. This may be due to solvent compatibility issue between the various pretreatments and the Crosslink primer system. Topcoated Crosslink primer system works best when the pretreatment coating is CCC. Therefore, the Crosslink primer system can eliminate the majority of Cr(VI) present in current chromate military coatings excluding the pretreatment coating (CCC).

**15. SUBJECT TERMS**
Hexavalent chromium (Cr(VI)), Chromate conversion coating (CCC), Trivalent chromium pretreatment (TCP), 2,5-dimercapto-1,3,4-thiadiazole (DMcT)

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# TABLE OF CONTENTS


| | | |
|---|---|---|
| TABLE OF CONTENTS | | p. ii |
| LIST OF FIGURES | | p. v |
| LIST OF TABLES | | p. xiv |
| LIST OF ACRONYMS | | p. xvii |
| ACKNOWLEDGEMENTS | | p. xix |
| EXECUTIVE SUMMARY | | p. xx |
| **1.0** | **INTRODUCTION** | p. 1 |
| 1.1 | Background | p. 1 |
| 1.1.1 | Corrosion Processes | p. 1 |
| 1.1.2 | Corrosion Protection with Smart Coatings and/or Inhibitors | p. 2 |
| 1.2 | Objective(s) of the Laboratory Studies | p. 4 |
| 1.3 | Regulatory Drivers | p. 5 |
| **2.0** | **DEMONSTRATION TECHNOLOGY** | p. 6 |
| 2.1 | Technology Description | p. 6 |
| 2.2 | Technology Development | p. 7 |
| 2.3 | Advantages and Limitations of Technology | p. 10 |
| 2.4 | Performance Objectives | p. 11 |
| **3.0** | **TEST DESIGN** | p. 13 |
| 3.1 | Laboratory Testing | p. 13 |
| 3.1.1 | Adhesion Testing | p. 13 |
| 3.1.1.2 | Crosshatch Adhesion | p. 13 |
| 3.1.1.3 | X-Cut Tape Adhesion | p. 16 |
| 3.1.1.4 | Wet-Tape Adhesion | p. 16 |
| 3.1.1.5 | Pull-off Adhesion ASTM D 4541 PATTI | p. 16 |
| 3.1.2 | Accelerated Weathering Tests | p. 19 |
| 3.1.2.1 | Neutral Salt Spray (NSS) Exposure | p. 19 |
| 3.1.2.2 | Accelerated Corrosion Test (GM9540P) | p. 21 |
| 3.1.2.3 | Moist Sulfur Dioxide ($SO_2$) Tests | p. 26 |
| 3.1.2.4 | Filiform Corrosion Resistance of Organic Coating Testing | p. 26 |
| 3.1.3 | Additional Laboratory Testing | p. 26 |
| 3.1.3.1 | Pencil Hardness | p. 26 |

3.1.3.2 Impact Flexibility Testing p. 27
3.1.3.3 Hydraulic, Lubricating Oil and JP-8 Fluid Resistance p. 27
3.1.3.4 Physical Requirement: Surface Appearance p. 28
3.1.3.5 Physical Requirement: Odor p. 28
3.1.3.6 Physical Requirement: Drying Time p. 28
3.1.3.7 Reparability Testing p. 29

**4.0 PERFORMANCE ASSESSMENT** p. 29

4.1 Laboratory Testing p. 29
4.1.1 **Laboratory Testing at WPAFB**
4.1.1.2 Adhesion Testing of Crosslink Primer Systems p. 29
4.1.1.2.1 ASTM D 3359, Method B, Crosshatch Adhesion p. 29
4.1.1.2.2 FTMS 141D, Method 6301, Wet-Tape Adhesion p. 32
4.1.1.2.3 ASTM D 4541 PATTI, Pull-off Adhesion p. 37
4.1.1.3 Accelerated Weathering Testing of Crosslink Primer Systems p. 39
4.1.1.3.1 Neutral Salt Spray (NSS) Testing p. 39
4.1.1.3.2 GM9540P Accelerated Corrosion Test p. 55
4.1.1.4 Additional Testing of Crosslink Primer Systems p. 66
4.1.1.4.1 ASTM D 3363 Pencil Hardness p. 66
4.1.1.4.2 Physical Requirement: Surface Appearance (MIL-PRF-32239) p. 68
4.1.1.4.3 Physical Requirement: Odor (MIL-PRF-32239) p. 68
4.1.1.4.4 Physical Requirement: Drying Time (MIL-PRF-32239) p. 69
4.1.1.4.5 Reparability Testing of the Crosslink Primer p. 69
4.1.1.5 **WPAFB Conclusions for Crosslink Primer Performance** p. 77
4.1.2 **Laboratory Testing at ARL** p. 78
4.1.2.1 Adhesion Studies on Crosslink Primer Systems p. 78
4.1.2.2 Accelerated Weathering Studies on Crosslink Primer Systems p. 79
4.1.2.2.1 Neutral Salt Spray Testing of Crosslink Primer Systems p. 79
4.1.2.2.2 GM9540P Accelerated Corrosion Test p. 81
4.1.2.3 **ARL Conclusions for Crosslink Primer Performance** p. 90
4.1.3 **Laboratory Testing at NAWCAD/NAWCWD** p. 90
4.1.3.1 Adhesion Testing for Crosslink Primer Systems p. 91
4.1.3.1.1 Crosshatch Adhesion Testing of Crosslink Primer Systems p. 91
4.1.3.1.2 Wet-tape Adhesion Testing of Crosslink Primer Systems p. 97
4.1.3.2 Accelerated Weathering Studies of Crosslink Primer System p. 102
4.1.3.2.1 Neutral Salt Spray Testing p. 102
4.1.3.2.2 $SO_2$ Corrosion Testing p. 112
4.1.3.2.3 Filiform Testing p. 120
4.1.3.3 Additional Testing for Crosslink Primer Systems p. 129
4.1.3.3.1 Fluid Resistance Testing for Crosslink Primer Systems p. 129
4.1.3.2.4 **NAWCAD/NAWCAD Conclusions for Crosslink** p. 129

| | | |
|---|---|---|
| | **Primer Systems** | |
| **4.1.4** | **Laboratory Testing at Crosslink** | p. 130 |
| 4.1.4.1 | Preparation Method for Crosslink Inhibitor | p. 130 |
| 4.1.4.2 | Adhesion Studies of Crosslink Primer Systems | p. 132 |
| 4.1.4.2.1 | Crosshatch Adhesion Studies of Crosslink Primer | p. 133 |
| 4.1.4.2.2 | Wet Tape Adhesion Studies of Crosslink Primer | p. 136 |
| 4.1.4.3 | Neutral Salt Spray Results of Crosslink Primer Systems | p. 139 |
| 4.1.4.4 | Additional Tests for Crosslink Primer Systems | p. 145 |
| 4.1.4.4.1 | Solvent Resistance Tests for Crosslink Primer Systems | p. 145 |
| 4.1.4.4.2 | GE Impact Flexibility Tests for Crosslink Primer Systems | p. 148 |
| **4.1.4.3** | **Conclusions of Laboratory Testing Performed by Crosslink** | p. 150 |
| **5.0** | **COST ASSESSMENT** | p. 152 |
| **6.0** | **REFERENCES** | p. 153 |
| **7.0** | **LIST OF PAPERS/PRESENTATIONS** | p. 155 |
| **APPENDIX A:** | **POINTS OF CONTACT** | p. 156 |

# LIST OF FIGURES


| | | |
|---|---|---|
| **Figure 1**: | DMcT (depicted above as $D^-$) reductively released by corrosion processes on AA 2024-T3 | p. 3 |
| **Figure 2**: | Cyclic Voltammetry of DMcT. Scan rate = 20 m/s | p. 8 |
| **Figure 3**: | DMcT release scheme | p. 8 |
| **Figures 4A and 4B**: | SVET scan of UV cured PANI-DMcT/poly(DMcT) formulation. Circles depict pin holes (anodic areas are positive volts, cathodic negative) | p. 9 |
| **Figure 5**: | SVET scans of PANI-DMcT coated on AA 2024T-3 | p. 9 |
| **Figure 6**: | Comparison of representative 2k epoxy formulations after ASTM B117 neutral salt fog spray exposure | p. 10 |
| **Figure 7**: | ASTM D 3359, Method B, Crosshatch Adhesion Rating Scale Description | p. 14 |
| **Figure 8**: | ASTM D 3359, Method B, Crosshatch Adhesion Visual Standard Reference Image | p. 15 |
| **Figure 9**: | Hydraulic Adhesion Test Equipment and Dolly configuration | p. 19 |
| **Figure 10**: | Rating Scale from ASTM D 714 | p. 25 |
| **Figure 11**: | ASTM D 3363 Pencil Hardness Rating System | p. 26 |
| **Figure 12**: | Primer-Only Samples on AA2024-T3, Wet Tape Adhesion Test Results: Pretreatment, Non-Chromated Coating, BAM-PPV (Repeated Testing) | p. 36 |
| **Figure 13**: | Topcoated Salt Spray Samples on AA2024-T3, Wet Tape Adhesion Test Results: Pretreatment, Non-Chromated Coating, BAM-PPV (Repeated Testing) | p. 36 |
| **Figure 14**: | Primer-Only Salt Spray Samples on AA2024-T3 after 2000 hours of Exposure: Pretreatment, Chromated Conversion Coating, Alodine 1600 | p. 43 |
| **Figure 15**: | Primer-Only Salt Spray Samples on AA7075-T6 after 2000 hours of Exposure: Pretreatment, Chromated Conversion Coating, Alodine 1600 | p. 43 |
| **Figure 16**: | Primer-Only Salt Spray Samples on AA2024-T3 after 2000 hours of Exposure: Pretreatment, Non-Chromated Conversion Coating, Alodine 5200 | p. 43 |
| **Figure 17**: | Primer-Only Salt Spray Samples on AA7075-T6 after 2000 hours of Exposure: Pretreatment, Non-Chromated Conversion Coating, Alodine 5200 | p. 44 |
| **Figure 18**: | Primer-Only Salt Spray Samples on AA2024-T3 after 2000 hours of Exposure: Pretreatment, Non-Chromated Coating, BAM-PPV | p. 45 |
| **Figure 19**: | Primer-Only Salt Spray Samples on AA7075-T6 after 2000 hours of Exposure: Pretreatment, Non-Chromated Coating, BAM-PPV | p. 45 |

**Figure 20**: Primer-Only Salt Spray Samples on AA2024-T3 after 2000 hours of Exposure: Pretreatment, Non-Chromated Surface Pretreament, PreKote p. 46
**Figure 21**: Primer-Only Salt Spray Samples on AA7075-T6 after 2000 hours of Exposure: Pretreatment, Non-Chromated Surface Pretreatment, PreKote p. 46
**Figure 22**: Topcoated Salt Spray Samples on AA2024-T3 after 2000 hours of Exposure: Pretreatment, Chromated Conversion Coating, Alodine 1600 p. 47
**Figure 23**: Topcoated Salt Spray Samples on AA7075-T6 after 2000 hours of Exposure: Pretreatment, Chromated Conversion Coating, Alodine 1600 p. 47
**Figure 24**: Topcoated Salt Spray Samples on AA2024-T3 after 2000 hours of Exposure: Pretreatment, Non-Chromated Conversion Coating, Alodine 5200 p. 48
**Figure 25**: Topcoated Salt Spray Samples on AA7075-T6 after 2000 hours of Exposure: Pretreatment, Non-Chromated Conversion Coating, Alodine 5200 p. 48
**Figure 26**: Topcoated Salt Spray Samples on AA2024-T3 after 2000 hours of Exposure: Pretreatment, Non-Chromated Coating, BAM-PPV p. 49
**Figure 27**: Topcoated Salt Spray Samples on AA7075-T6 after 2000 hours of Exposure: Pretreatment, Non-Chromated Coating, BAM-PPV p. 49
**Figure 28**: Topcoated Salt Spray Samples on AA2024-T3 after 2000 hours of Exposure: Pretreatment, Non-Chromated Surface Pretreament, PreKote p. 50
**Figure 29**: Topcoated Salt Spray Samples on AA7075-T6 after 2000 hours of Exposure: Pretreatment, Non-Chromated Surface Pretreatment, PreKote p. 50
**Figure 30**: Primer-Only Salt Spray Samples on AA2024-T3 after 500 hours of Exposure: Pretreatment, Chromated Conversion Coating, Alodine 1600 (Repeated Testing) p. 53
**Figure 31**: Primer-Only Salt Spray Samples on AA2024-T3 after 500 hours of Exposure: Pretreatment, Non-Chromated Coating, BAM-PPV (Repeated Testing) p. 53
**Figure 32**: Topcoated Salt Spray Samples on AA2024-T3 after 500 hours of Exposure: Pretreatment, Chromated Conversion Coating, Alodine 1600 (Repeated Testing) p. 54
**Figure 33**: Topcoated Salt Spray Samples on AA2024-T3 after 500 hours of Exposure: Pretreatment, Non-Chromated Coating, BAM-PPV (Repeated Testing) p. 54

**Figure 34**: Primer-Only Samples on 4130N steel after 40 cycles of GM9540P Exposure: Pretreatment, Cadmium Plate per QQ-P-416 p. 60
**Figure 35**: Primer-Only Samples on 1010 steel after 40 cycles of GM9540P Exposure: Pretreatment, Cadmium Plate per QQ-P-416 p. 60
**Figure 36**: Primer-Only Samples on 4130N steel after 40 cycles of GM9540P Exposure: No Pretreatment, Surface Cleaning Only p. 61
**Figure 37**: Primer-Only Samples on 1010 steel after 40 cycles of GM9540P Exposure: No Pretreatment, Surface Cleaning Only p. 61
**Figure 38**: Primer-Only Samples on 4130N steel after 40 cycles of GM9540P Exposure: Pretreatment, Non-Chromated Coating, BAM-PPV p. 62
**Figure 39**: Primer-Only Samples on 1010 steel after 40 cycles of GM9540P Exposure: Pretreatment, Non-Chromated Coating, BAM-PPV p. 62
**Figure 40**: Topcoated Samples on 4130N steel after 40 cycles of GM9540P Exposure: Pretreatment, Cadmium Plate per QQ-P-416 p. 63
**Figure 41**: Topcoated Samples on 1010 steel after 40 cycles of GM9540P Exposure: Pretreatment, Cadmium Plate per QQ-P-416 p. 63
**Figure 42**: Topcoated Samples on 4130N steel after 40 cycles of GM9540P Exposure: No Pretreatment (Surface Cleaning Only) p. 64
**Figure 43**: Topcoated Samples on 1010 steel after 40 cycles of GM9540P Exposure: No Pretreatment (Surface Cleaning Only) p. 64
**Figure 44**: Topcoated Samples on 4130N steel after 40 cycles of GM9540P Exposure: Pretreatment, Non-Chromated Coating, BAM-PPV p. 65
**Figure 45**: Topcoated Samples on 1010 steel after 40 cycles of GM9540P Exposure: Pretreatment, Non-Chromated Coating, BAM-PPV p. 65
**Figure 46**: Primary Coating System Application for Reparability Samples p. 71
**Figure 47**: Coating System Removal for Reparability Testing p. 72
**Figure 48**: Coating System Interfaces for Adhesion Testing in the Reparability Test p. 73
**Figure 49**: Locations for Interfaces, Adhesion Testing in the Reparability Test p. 74
**Figure 50**: Crosslink direct to metal, DoD-P-15328 with Crosslink primer, Crosslink as pretreatment with MIL-PRF-53022, and p. 80

DoD-P-15328 with MIL-PRF-53022
following NSS exposure

**Figure 51**: AA 2024-T3 panels Pretreated with Alodine 1200 and topcoated with MIL-PRF-85285. Primers are MIL-PRF-23377C, MIL-PRF-23377N, and Crosslink following 120 cycles GM 9540 exposure p. 82

**Figure 52**: AA 2024 panels Pretreated with Sur Tec 650 and topcoated with MIL-PRF-85285. Primers are MIL-PRF-23377C, MIL-PRF-23377N, and Crosslink following 120 cycles GM 9540 exposure p. 83

**Figure 53**: AA 2024-T3 panels pretreated with BAM-PPV and topcoated with MIL-PRF-85285. Primers are MIL-PRF-23377C @120 cycles, MIL-PRF-23377N, @120 cycles and Crosslink @20 cycles p. 84

**Figure 54**: AA 2024-T3 panels with BAM-PPV/MIL-PRF-53022, BAM-PPV/Crosslink primer, Alodine 5700/MIL-PRF-53022, and Alodine 5700/Crosslink primer. All are topcoated with MIL-DTL-64159. Images are following120 cycles GM 9540 except BAM-PPV/Crosslink which was taken following 20 cycles p. 85

**Figure 55**: AA 2024-T3 panels Pretreated with Alodine 1200 and Topcoated with MIL-PRF-85285. Primers are MIL-PRF-23377C, MIL-PRF-23377N, and Crosslink following 120 cycles GM 9540 exposure p. 87

**Figure 56**: AA 7075-T6 panels pretreated with Sur Tec 650 and topcoated with MIL-PRF-85285. Primers are MIL-PRF-23377C, MIL-PRF-23377N, and Crosslink following 120 cycles GM 9540 exposure p. 88

**Figure 57**: Crosslink direct to metal, DoD-P-15328 with Crosslink primer, Crosslink as pretreatment with MIL-PRF-53022, and DoD-P-15328 with MIL-PRF-53022 following 20 cycles GM 9540 exposure p. 89

**Figure 58**: Dry Adhesion Results per ASTM D 3359, Method B p. 91

**Figure 59**: AA2024-T3 – SurTec 650 + 23377C + 85285 (ASTM D3359, Method B) p. 92

**Figure 60**: AA7075-T6 SurTec 650 + 23377C + 85285 (ASTM D3359, Method B) p. 92

**Figure 61**: AA2024-T3 SurTec 650 + 23377N + 85285 (ASTM D3359, Method B) p. 92

**Figure 62**: AA7075-T6 SurTec 650 + p. 93

23377N + 85285 (ASTM D3359, Method B)
**Figure 63**: AA2024-T3 SurTec 650 + Crosslink + 85285 (ASTM D3359, Method B) p. 93
**Figure 64**: AA7075-T6 SurTec 650 + Crosslink + 85285 (ASTM D3359, Method B) p. 93
**Figure 65**: AA2024-T3 Alodine 1200S + 23377C + 85285 (ASTM D3359, Method B) p. 94
**Figure 66**: AA7075-T6 Alodine 1200S + 23377C + 85285 (ASTM D3359, Method B) p. 94
**Figure 67**: AA2024-T3 Alodine 1200S + 23377N + 85285 (ASTM D3359, Method B) p. 94
**Figure 68**: AA7075-T6 Alodine 1200S + 23377N + 85285 (ASTM D3359, Method B) p. 95
**Figure 69**: AA2024-T3 Alodine 1200S + Crosslink + 85285 (ASTM D3359, Method B) p. 95
**Figure 70**: AA7075-T6 Alodine 1200S + Crosslink + 85285 (ASTM D3359, Method B) p. 95
**Figure 71**: AA2024-T3 BAM-PPV + 23377C + 85285 (ASTM D3359, Method B) p. 96
**Figure 72**: AA7075-T6 BAM-PPV + 23377C + 85285 (ASTM D3359, Method B) p. 96
**Figure 73**: AA2024-T3 BAM-PPV + 23377N + 85285 (ASTM D3359, Method B) p. 96
**Figure 74**: AA7075-T6 BAM-PPV + 23377N + 85285 (ASTM D3359, Method B) p. 97
**Figure 75**: AA2024-T3 BAM-PPV + Crosslink + 85285 (ASTM D3359, Method B) p. 97
**Figure 76**: AA7075-T6 BAM-PPV + Crosslink + 85285 (ASTM D3359, Method B) p. 97
**Figure 77**: Wet Tape Adhesion Results per ASTM D 3359 p. 98
**Figure 78**: AA2024-T3 SurTec 650 + 23377C + 85285 (1-Day Wet Adhesion) p. 98
**Figure 79**: AA7075-T6 SurTec 650 + 23377C + 85285 (1-Day Wet Adhesion) p. 98
**Figure 80**: AA2024-T3 SurTec 650 + 23377N + 85285 (1-Day Wet Adhesion) p. 99
**Figure 81**: AA7075-T6 SurTec 650 + 23377N + 85285 (1-Day Wet Adhesion) p. 99
**Figure 82**: AA2024-T3 SurTec 650 + Crosslink + 85285 (1-Day Wet Adhesion) p. 99
**Figure 83**: AA7075-T6 SurTec 650 + Crosslink + 85285 (1-Day Wet Adhesion) p. 99
**Figure 84**: AA2024-T3 Alodine 1200S + 23377C + 85285 (1-Day Wet Adhesion) p. 99

**Figure 85**: AA7075-T6 Alodine 1200S + 23377C + 85285 (1-Day Wet Adhesion) p. 100
**Figure 86**: AA2024-T3 Alodine 1200S + 23377N + 85285 (1-Day Wet Adhesion) p. 100
**Figure 87**: AA7075-T6 Alodine 1200S + 23377N + 85285 (1-Day Wet Adhesion) p. 100
**Figure 88**: AA2024-T3 Alodine 1200S + Crosslink + 85285 (1-Day Wet Adhesion) p. 100
**Figure 89**: AA7075-T6 Alodine 1200S + Crosslink + 85285 (1-Day Wet Adhesion) p. 100
**Figure 90**: AA2024-T3 BAM-PPV + 23377C + 85285 (1-Day Wet Adhesion) p. 101
**Figure 91**: AA7075-T6 BAM-PPV + 23377C + 85285 (1-Day Wet Adhesion) p. 101
**Figure 92**: AA2024-T3 BAM-PPV + 23377N + 85285 (1-Day Wet Adhesion) p. 101
**Figure 93**: AA7075-T6 BAM-PPV + 23377N + 85285 (1-Day Wet Adhesion) p. 101
**Figure 94**: AA2024-T3 BAM-PPV + Crosslink + 85285 (1-Day Wet Adhesion) p. 101
**Figure 95**: AA7075-T6 BAM-PPV + Crosslink + 85285 (1-Day Wet Adhesion) p. 102
**Figure 96**: AA2024-T3 Alodine 1200S + 23377C + 85285 (3000 hours NSS) p. 104
**Figure 97**: AA7075-T6 Alodine 1200S + 23377C + 85285 (3000 hours NSS) p. 104
**Figure 98**: AA2024-T3 Alodine 1200S + 23377N + 85285 (3000 hours NSS) p. 105
**Figure 99**: AA7075-T6 Alodine 1200S + 23377N + 85285 (3000 hours NSS) p. 105
**Figure 100**: AA2024-T3 Alodine 1200S + Crosslink + 85285 (3000 hours NSS) p. 106
**Figure 101**: AA7075-T6 Alodine 1200S + Crosslink + 85285 (3000 hours NSS) p. 106
**Figure 102**: AA2024-T3 BAM-PPV + 23377C + 85285 (3000 hours NSS) p. 107
**Figure 103**: AA2024-T3 BAM-PPV + 23377N + 85285 (3000 hours NSS) p. 107
**Figure 104**: AA7075-T6 BAM-PPV + 23377N + 85285 (3000 hours NSS) p. 108
**Figure 105**: AA2024-T3 BAM-PPV + Crosslink + 85285 (3000 hours NSS) p. 108
**Figure 106**: AA7075-T6 BAM-PPV + Crosslink + 85285 (3000 hours NSS) p. 109
**Figure 107**: AA2024-T3 SurTec 650 + 23377C + 85285 (3000 hours NSS) p. 109

**Figure 108**: AA7075-T6 SurTec 650 + 23377C + 85285 (3000 hours NSS) p. 110
**Figure 109**: AA2024-T3 SurTec 650 + 23377N + 85285 (3000 hours NSS) p. 110
**Figure 110**: AA7075-T6 SurTec 650 + 23377N + 85285 (3000 hours NSS) p. 111
**Figure 111**: AA2024-T3 SurTec 650 + Crosslink + 85285 (3000 hours NSS) p. 111
**Figure 112**: AA7075-T6 SurTec 650 + Crosslink + 85285 (3000 hours NSS) p. 112
**Figure 113**: AA2024-T3 Alodine 1200S + 23377C + 85285 (1500 hours ASTM G85, A4) p. 114
**Figure 114**: AA7075-T6 Alodine 1200S + 23377C + 85285 (1500 hours ASTM G85, A4) p. 114
**Figure 115**: AA2024-T3 Alodine 1200S + 23377N + 85285 (1500 hours ASTM G85, A4) p. 115
**Figure 116**: AA7075-T6 Alodine 1200S + 23377N + 85285 (1500 hours ASTM G85, A4) p. 115
**Figure 117**: AA2024-T3 Alodine 1200S + Crosslink + 85285 (1500 hours ASTM G85, A4) p. 115
**Figure 118**: AA7075-T6 Alodine 1200S + Crosslink + 85285 (1500 hours ASTM G85, A4) p. 116
**Figure 119**: AA2024-T3 BAM-PPV + 23377C + 85285 (1500 hours ASTM G85, A4) p. 116
**Figure 120**: AA7075-T6 BAM-PPV + 23377C + 85285 (1500 hours ASTM G85, A4) p. 116
**Figure 121**: AA2024-T3 BAM-PPV + 23377N + 85285 (1500 hours ASTM G85, A4) p. 117
**Figure 122**: AA7075-T6 BAM-PPV + 23377N + 85285 (1500 hours ASTM G85, A4) p. 117
**Figure 123**: AA2024-T3 BAM-PPV + Crosslink + 85285 (1500 hours ASTM G85, A4) p. 117
**Figure 124**: AA7075-T6 BAM-PPV + Crosslink + 85285 (1500 hours ASTM G85, A4) p. 118
**Figure 125**: AA2024-T3 SurTec 650 + 23377C + 85285 (1500 hours ASTM G85, A4) p. 118
**Figure 126**: AA7075-T6 SurTec 650 + 23377C + 85285 (1500 hours ASTM G85, A4) p. 118
**Figure 127**: AA2024-T3 SurTec 650 + 23377N + 85285 (1500 hours ASTM G85, A4) p. 119
**Figure 128**: AA7075-T6 SurTec 650 + 23377N + 85285 (1500 hours ASTM G85, A4) p. 119
**Figure 129**: AA2024-T3 SurTec 650 + Crosslink + 85285 (1500 hours ASTM G85, A4) p. 119
**Figure 130**: AA7075-T6 SurTec 650 + Crosslink + 85285 (1500 hours ASTM G85, A4) p. 120

**Figure 131**: AA2024-T3 Alodine 1200S + 23377C + 85285 (ASTM D 2803) p. 122
**Figure 132**: AA7075-T6 Alodine 1200S + 23377C + 85285 (ASTM D 2803) p. 122
**Figure 133**: AA2024-T3 Alodine 1200S + 23377N + 85285 (ASTM D 2803) p. 123
**Figure 134**: AA7075-T6 Alodine 1200S + 23377N + 85285 (ASTM D 2803) p. 123
**Figure 135**: AA2024-T3 Alodine 1200S + Crosslink + 85285 (ASTM D 2803) p. 123
**Figure 136**: AA7075-T6 Alodine 1200S + Crosslink + 85285 (ASTM D 2803) p. 124
**Figure 137**: AA2024-T3 SurTec 650 + 23377C + 85285 (ASTM D 2803) p. 124
**Figure 138**: AA7075-T6 SurTec 650 + 23377C + 85285 (ASTM D 2803) p. 124
**Figure 139**: AA2024-T3 – SurTec 650 + 23377N + 85285 (ASTM D 2803) p. 125
**Figure 140**: AA7075-T6 SurTec 650 + 23377N + 85285 (ASTM D 2803) p. 125
**Figure 141**: AA2024-T3 SurTec 650 + Crosslink + 85285 (ASTM D 2803) p. 126
**Figure 142**: AA7075-T6 SurTec 650 + Crosslink + 85285 (ASTM D 2803) p. 126
**Figure 143**: AA2024-T3 BAM-PPV + 23377C + 85285 (ASTM D 2803) p. 127
**Figure 144**: AA7075-T6 BAM-PPV + 23377C + 85285 (ASTM D 2803) p. 127
**Figure 145**: AA2024-T3 BAM-PPV + 23377N + 85285 (ASTM D 2803) p. 127
**Figure 146**: AA7075-T6 BAM-PPV + 23377N + 85285 (ASTM D 2803) p. 128
**Figure 147**: AA2024-T3 BAM-PPV + Crosslink + 85285 (ASTM D 2803) p. 128
**Figure 148**: AA7075-T6 BAM-PPV + Crosslink + 85285 (ASTM D 2803) p. 128
**Figure 149**: BoeAero (25% Corrlink 30A-lab scale, Primer only) on AA 2024-T3 after 8500 hours NSS p. 141
**Figure 150**: BoeAero (25% InhibiCor 1000 – pilot scale, Primer only) on AA 2024-T3 after 8500 hours NSS p. 141
**Figure 151**: ESTCP 7.5/5 (BoeAero TC, Primer only) on AA 2024-T3 after 2500 hours NSS p. 142
**Figure 152**: Deft Non-chromate on AA 2024-T3 after 2500 hours NSS p. 142
**Figure 153**: Deft Chromate Control on AA 2024-T3 after 3000 hours NSS p. 143

**Figure 154**: ESTCP 7.5/5, (BoeAero Topcoated) on AA 2024-T3 after 2500 hours NSS p. 143
**Figure 155**: Deft Non-Chromate on AA 2024-T3 after 2500 hours NSS p. 143
**Figure 156**: Deft Chromate Control on AA 2024-T3 after 3000 hours NSS p. 144
**Figure 157**: Commercial 3K Epoxy Resin, 25% InhibiCor 1000, Primer only on AA 2024-T3 after 5000 hours NSS p. 144
**Figure 158**: Deft Chromate Control on AA 2024-T3 after 5000 hours NSS p. 144

## LIST OF TABLES


| | | |
|---|---|---|
| **Table 1**: | Best/Worst Performing Crosslink Primer Formulation Coating Systems | p. xxii |
| **Table 2**: | Estimated Compliance Costs for General Industry with New Cr(VI) Guidelines | p. 5 |
| **Table 3**: | Performance Objectives for ESTCP Program WP 200904 | p. 12 |
| **Table 4**: | ASTM D 3359 Adhesion, Method A, Rating Scale | p. 16 |
| **Table 5**: | PATTI Coating Failure Descriptions | p. 18 |
| **Table 6**: | RXSSO Scribe Appearance Rating System | p. 20 |
| **Table 7**: | RXSSO Undercutting Rating System | p. 21 |
| **Table 8**: | Blistering Rating System (Modified from ASTM D 714) | p. 21 |
| **Table 9**: | Rating of Failure at Scribe (Procedure A) Representative Mean Creepage from Scribe | p. 23 |
| **Table 10**: | Rating Scale from ASTM D 610 | p. 24 |
| **Table 11**: | ASTM D 3359 Crosshatch Adhesion (Primed Systems) | p. 30 |
| **Table 12**: | ASTM D 3359 Crosshatch Adhesion (MIL-PRF-85285 Topcoated Systems) | p. 31 |
| **Table 13**: | FTMS 141, ASTM D 3359 Wet Tape Adhesion (Primed Systems) | p. 33 |
| **Table 14**: | FTMS 141, ASTM D 3359 Wet Tape Adhesion (MIL-PRF-85285 Topcoated Systems) | p. 34 |
| **Table 15**: | Systems Retested using BAM-PPV and Crosslink Corrosion-Inhibiting Primer | p. 35 |
| **Table 16**: | Results from Retest, Wet Tape Adhesion | p. 35 |
| **Table 17**: | ASTM D 4541 Pull-Off Adhesion (Primed Systems) | p. 37 |
| **Table 18**: | ASTM D 4541 Pull-Off Adhesion (MIL-PRF-85285 Topcoated Systems) | p. 38 |
| **Table 19**: | Salt Spray Ratings (2000 hours) (Primed Systems) | p. 40 |
| **Table 20**: | Salt Spray Ratings (2000 hours) using Alodine 1600 and 5200 Pretreatments (MIL-PRF-85285 Topcoated Systems) | p. 41 |
| **Table 21**: | Salt Spray Ratings (2000 hours) using BAM-PPV and Prekote Pretreatments (MIL-PRF-85285 Topcoated Systems) | p.42 |
| **Table 22**: | Primer-Only Salt Spray Ratings (500 hours) (Repeated Testing) | p. 52 |
| **Table 23**: | Salt Spray Ratings (500 hours) (MIL-PRF-85285 Topcoated Systems) (Repeated Testing) | p. 52 |
| **Table 24**: | GM9540P Accelerated Corrosion on 4130N Steel, Solvent-Cleaned Samples (Primer-Only Systems) | p. 56 |
| **Table 25**: | GM9540P Accelerated Corrosion on 4130N Steel, Solvent-Cleaned Samples (MIL-PRF-85285 Topcoated Systems) | p. 57 |

**Table 26**: GM9540P Accelerated Corrosion on 1010 Cold-Rolled Steel, Solvent-Cleaned Samples (Primer-Only Systems) p. 58
**Table 27**: GM9540P Accelerated Corrosion on 1010 Cold-Rolled Steel, Solvent-Cleaned Samples (MIL-PRF-85285 Topcoated Systems) p. 59
**Table 28**: ASTM D 3363 Pencil Hardness (Primed Systems) p. 66
**Table 29**: ASTM D 3363 Pencil Hardness (MIL-PRF-85285 Topcoated Systems) p. 67
**Table 30**: Reparability Testing for AA2024-T3 (Bare 0.032 inches) p. 70
**Table 31**: Reparability Results, Color Data p. 74
**Table 32**: Reparability Results, Interface Adhesion Results p. 75
**Table 33**: Reparability Results, Interface Pencil Hardness Results p. 75
**Table 34**: ASTM D 3359 and ASTM D 3363 Results for Topcoated Coatings Systems p. 76
**Table 35**: Averaged pull-off adhesion values p. 79
**Table 36**: ASTM D 1654 ratings of low carbon steel with Crosslink as a pretreatment and primer in ASTM B 117 salt fog exposure p. 80
**Table 37**: ASTM D 1654 ratings for AA 2024-T3 with Alodine 1200 pretreatment and MIL-PRF-85285 topcoat p. 81
**Table 38**: ASTM D 1654 ratings for AA 2024 with Sur Tec 650 pretreatment and MIL-PRF- 85285 topcoat p. 82
**Table 39**: ASTM D 1654 ratings for AA 2024-T3 with Sur Tec 650 pretreatment and MIL-PRF- 85285 topcoat p. 84
**Table 40**: ASTM D 1654 ratings for Al 2024 with BAM-PPV and Alodine 1200 pretreatments, MIL-PRF-53022 and Crosslink primers and MIL-DTL-64159 topcoat p. 85
**Table 41**: ASTM D 1654 ratings of AA 7075-T6 with Alodine1200 pretreatment and MIL-PRF-85285 topcoat p. 86
**Table 42**: ASTM D 1654 ratings for AA 7075-T6 with Sur Tec 650 pretreatment and MIL-PRF- 85285 topcoat p. 87
**Table 43**: ASTM D 1654 ratings of low carbon steel with Crosslink as a pretreatment and primer in GM 9540 cyclic exposure p. 89
**Table 44**: NSS ASTM B117 Test Results p. 103
**Table 45**: ASTM G85, Annex 4 Test Results p. 113
**Table 46**: Filiform Testing Results per ASTM D 2803 p. 121
**Table 47**: Fluid Resistance Testing of Crosslink Primer Systems p. 129
**Table 48**: Cross-Hatch Adhesion Results (ESTCP U1) p. 133
**Table 49**: Cross-Hatch Adhesion Results (ESTCP FA1) p. 134
**Table 50**: Cross-Hatch Adhesion Results (ESTCP XL2) p. 135
**Table 51**: Wet-Tape Adhesion Results (ESTCP FA3) p. 137
**Table 52**: Wet-tape Adhesion Results (ESTCP XL2) p. 138

**Table 53**: Solvent Resistance Results for ESTCP U1 p. 146
**Table 54**: Solvent Resistance Results for ESTCP FA1/FA3 p. 147
**Table 55**: Solvent resistance Results for ESTCP XL2 p. 148
**Table 56**: Rating System for Evaluation of Impact-Flexibility Results p. 149
**Table 57**: GE Impact Flexibility Test Results p. 150
**Table 58**: Cost Comparison of Crosslink Primer to Cr(VI) Primer p. 152

# LIST OF ACRONYMS

| | |
|---|---|
| AA | Aluminum alloy |
| AF | Air Force |
| APC | Advanced Performance Topcoat |
| ARL | Army Research Laboratory |
| ASTM | American Standard Test Method |
| ATC | Aberdeen Test Center |
| BAM-PPV | poly(2,5-bis(N-methyl-N-hexylamino)phenylene vinylene) |
| BIF | Blisters in field |
| CARC | Chemical Agent Resistant Coating |
| CCC | Chromate conversion coating |
| Cr(VI) | Hexavalent chromium |
| CP | Conductive polymers |
| COTS | Cost off the Shelf |
| CV | Cyclic voltammetry |
| CRADA | Cooperative Research and Development Agreement |
| CTIO | Coatings Technology Integration Office |
| DOD | Department of Defense |
| D | Dopant |
| DMcT | 2,5-dimercapto-1,3,4-thiadiazole |
| EAP | Electroactive Polymers |
| ESOH | Environmental Safety Occupational Health |
| ESTCP | Environmental Security Technology Certification Program |
| EU | European Union |
| FTMS | Federal Test Method Standard |
| GM9540P | General Motors Accelerated corrosion test |
| HAPs | Hazardous Air Pollutants |
| HSS | High Strength Steel |
| HATE | Hydraulic Adhesion Test Equipment |
| HVLP | High Volume Low Pressure |
| ICP | Inherently conductive polymers |
| JTP | Joint Test Protocol |
| JTR | Joint Technical Report |
| MEK | Methyl ethyl ketone |
| MURI | Multidisciplinary University Research Initiative |
| NACE | National Association of Corrosion Engineers |
| NAWCAD | Naval Air Warfare Center Aircraft Division |
| NAWCWD | Naval Air Warfare Center Weapons Division |
| N/A | Not available |
| NIOSH | National Institute for Occupational Safety and Health |
| NSS | Neutral salt spray |
| OEM | Original Equipment Manufacturer |
| Oxsol-100 | 4-chlorobenzotrifluoride or 1-chloro-4-(trifluoromethyl)benzene |
| ORR | Oxygen reduction reaction |

| | |
|---|---|
| PANI | Polyaniline |
| PATTI | Pneumatic adhesion tensile test instrument |
| % | Percent |
| PPE | Protective personnel equipment |
| PPy | Poly(pyrrole) |
| PT | Poly(thiophene) |
| rt | room temperature |
| REACH | Registration Evaluation Authorization and Restriction of Chemicals |
| RXSSO | Logistics Systems Support Branch Office |
| SERDP | Strategic Environmental Research and Development Program |
| SVHC | Substance of Very High Concern |
| $SO_2$ | Sulfur dioxide corrosion test |
| TCP | Trivalent Chromium Pretreatment |
| TWA | Time Weighted Average |
| UDRI | University of Dayton Research Institute |
| UV | Ultra-violet |
| VOC | Volatile Organic compounds |
| WPAFB | Wright Patterson Air Force Base |
| WTA | Wet Tape Adhesion |
| wt% | Weight percent |

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Dr. Peter Zarras directed the overall project, synthesized polymer and coated coupons with poly(2,5-bis(N-methyl-N-hexylamino)phenylene vinylene) (BAM-PPV) solution. Ms. Cindy Webber helped in the development and implementation of the test matrix for BAM-PPV and crosslink primer formulations.

Drs. Ramil Marcelo L. Mercado, George Koustis, Patrick J. Kinlen, Scott Hayes and Mr. Michael Kiely, Mr. Frank Doering and Mr. John Fury synthesized, formulated, coated and tested various coating combinations using the Crosslink primer for adhesion and in accelerated weathering chambers.

Ms. Diane Buhrmaster managed the laboratory testing for the Crosslink primer coated coupons at WPAFB. The testing performed at WPAFB were adhesion, accelerated weathering and reparability.

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Ms. Amy L. Fowler coated the Crosslink primer in various combinations with pretreatment, topcoats and supplied coated coupons to ARL and NAWCWD for testing. The NAWCAD tested these Crosslink coating systems for adhesion and in accelerated weathering chambers.

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# EXECUTIVE SUMMARY

Current coating systems in use throughout the Department of Defense (DoD) utilize hexavalent chromium (Cr(VI) for the long-term protection of military weapons systems. These primers, while being extremely effective, are under significant pressure to be eliminated because they contain Cr(VI), a known carcinogen. Federal, state and local agencies have issued regulations that limit or prohibit the use of chromate materials. The use of Cr(VI) compounds is tightly controlled by the Environmental Protection Agency (EPA) regulations issued under the Toxic Substances Control Act, Safe Drinking Water Act, Clean Water Act, Clean Air Act, Resource Conservation Recovery Act, Comprehensive Environmental Response, and by the Occupational Safety Health Administration (OSHA). OSHA regulates the amount of Cr(VI) to which workers can be exposed. Environmental regulations have recently reduced the permissible exposure levels (PEL) of Cr(VI) over an 8-hour time-weighted average (TWA) work period to be no more than 5 micrograms per cubic meter (5 $\mu g/m^3$) effective as of January 2006. This regulation also includes provisions for employee protection such as preferred methods for controlling exposure, respiratory protection, protective work clothing and equipment, hygiene areas and practices, medical surveillance, hazard communication, and record keeping. This reduced level of exposure is difficult for many maintenance organizations to meet without adding significant operational costs.

In order to prevent compromise to weapon system corrosion control, a replacement for fully chromated coating systems (chromate pretreatment + chromate primer) that provides similar protection is needed. This ESTCP program sought to combine the technology from previous non-chromated coating studies to build a coating system that is tested and available for use by the military services to protect weapon systems. The end goal is to fully eliminate chromates from military coating systems. Previous work sponsored by ESTCP office (ESTCP WP Program # 200527) and NAWCAD CPC program builds upon previous conductive polymer (CP) also commonly referred to as electroactive polymers (EAP) studies. These two programs were coordinated through the NAWCWD at China Lake. These studies were conducted in cooperation with the Army Research Laboratory (ARL) and the Air Force Research Laboratory Coatings Technology Integration Office (AFRL/RXSSO CTIO) as well as industry partner Crosslink USA (Crosslink). This current ESTCP program (WP Project # 200904) seeks to combine the technology that utilizes the conductive pigment formulated by Crosslink in epoxy formulations with Cr(VI)-free pretreatments to generate a multifunctional coating system that can fully eliminate chromates from military coating systems. **This two-year laboratory study optimized the Crosslink inhibitor in epoxy formulations and showed compatibility with non-chromate pretreatments and topcoats for a full non-Cr(VI) military coating system. The best performing system has been transitioned to a new ESTCP demonstration/validation program for eventual field testing.**

A recent MURI (Multidisciplinary University Research Initiative) study has strongly suggested that Cr(VI) within coatings primers could be providing corrosion inhibition through a “smart release” of Cr(VI) to inhibit corrosion within pinholes and other flaws. The release is in response to electrochemical changes at the metal surface. One hypothesis is that Cr(VI) acts to inhibit the oxygen reduction reaction (ORR) that

serves as one driver of corrosion. The implication is that one characteristic of any replacement primer is that it must be able to protect aluminum in coating pinholes and flaws, as well as in severe environments such as salt spray encountered by aircraft located near the sea or on aircraft carriers.

Crosslink has developed a Cr(VI)-free epoxy primer using corrosion-inhibiting compounds (2,5-dimercapto-1,3,4-thiadiazole, DMcT) that have been demonstrated to mimic the corrosion inhibiting properties of Cr(VI). A two-year Environmental Security Technology Certification Program (ESTCP) (WP-200904) FY10-11 was undertaken to prove the viability of this new compound. The tests were performed to access the non-chromium Crosslink coating compatibility with alternative pretreatment coatings and topcoats. Each service, WPAFB, ARL and NAWCWD/NAWCAD and Crosslink tested BAM-PPV, trivalent chromium pretreatment (TCP), CCC and Prekote pretreatments with and without topcoats and the non-chromate Crosslink inhibitor formulations. Each service conducted specific laboratory tests to evaluate the Crosslink primer performance with various pretreatments and in full military coatings (topcoat). Chromated coatings were used as the controls for all accelerated weathering tests. **Each service tested the Crosslink primer formulation as an alternative to Cr(VI) primer systems according to their military coating specification. Each service had specific testing done in order to evaluate the performance of the Crosslink primer for eventual transition to the "Comprehensive Evaluation and Transition of Non-Chromated Paint Primers" ESTCP Project WP-201132.**

**After each facility tested the non-chromate Crosslink primer and it passed their performance requirements the material was transitioned to ESTCP WP Project # 201132. Therefore, it is beneficial to the reader to see that the testing performed by each organization is presented in specific sections in this report attributed to that organization. The table of contents reflects the specific testing done by each organization with final summations to provide the reader with take-away bullets describing the successes and failures of the Crosslink primer formulations with and without full military coatings.**

The results are reported by each facility. The laboratory tests were conducted with and without full military coatings containing Cr(VI) or nonchromium coatings in accelerated weathering chambers, adhesion testing, fluid resistance and additional tests. Table 1 highlights the best and worst performing Crosslink primer military coating for a variety of tests. The color codes found in Table 1 are as follows:

- Red = fail
- Green = pass
- Yellow = marginal performance

These color codes will be used throughout the text to help the reader understand which systems pass, fail or are marginal in their performance. Any additional color codes used throughout this Joint Technical Report (JTP) are identified.

**Table 1**: Best/Worst Performing Crosslink Primer Formulation Coating Systems

| Substrate | Pretreatment | Primer[a] | Topcoat[b] | NSS[c] | Adhesion[d] |
|---|---|---|---|---|---|
| AA 2024-T3 | CCC | Crosslink Primer (25% Corrlink 30A-lab scale) | X | 8500 hours (pass, scribed) | 4B[b] (pass) |
| AA 2024-T3 | CCC | Crosslink Primer (25% InhibiCor 1000-pilot scale) | X | 8500 hours (pass, scribed) | 4B (pass) |
| AA 2024-T3 | CCC | Commercial 3K epoxy Resin (25%InhibiCor 1000) | X | 5000 hours (pass, scribed) | 4B (pass) |
| AA 5182-T0 | CCC | Commercial 3K epoxy Resin (25% InhibiCor 1000) | X | 5000 hours (pass, scribed) | 4B (pass) |
| AA 2024-T3 | BAM-PPV | Crosslink Primer | MIL-PRF-85285 | Fail at 2000 hours Corrosion/blisters in scribe | 4B (pass) |
| AA 2024-T3 | CCC | Crosslink Primer | MIL-PRF-85285 | Marginal Performance at 2000 hours | 4B (pass) |
| Low Carbon Steel | DOD-P-15328 | Crosslink Primer | X | Similar Performance to DOD-P-15328 | NA |

a: Non-chromated primers
b: Aircraft polyurethane topcoat (MIL-PRF-85285) and Army solvent-borne topcoat (MIL-PRF-5302253039)
c: NSS = Neutral salt spray testing (ASTM B117)
d: Adhesion testing (ASTM D 3359)
NA: Not Available

The overall recommendation of the Crosslink primer in its various formulations by each of the services has been that the primer performs best with a chromate pretreatment coating, specifically CCC. Alternative pretreatments such as BAM-PPV, Prekote and TCP do not work with the Crosslink primer system as formulated. This may be due to solvent compatibility issue between the various pretreatments and the Crosslink primer system. Topcoated Crosslink primer system works best when the pretreatment coating is CCC. Therefore, the Crosslink primer system can eliminate the majority of Cr(VI) present in current chromate military coatings excluding the pretreatment coating (CCC).

The best performing Crosslink primer system was down selected at the end of FY11 and transitioned to the "Comprehensive Evaluation and Transition of Non-Chromated Paint Primers" ESTCP Project WP-201132. This current project is evaluating the best performing Crosslink primer system across the services and plans to select the best full military coating system containing the Crosslink primer. This coating system represents a viable alternative to Cr(VI) primer and will be field testing during FY14-16.

# 1.0 INTRODUCTION

## 1.1 Background

### 1.1.1 Corrosion Processes

A fundamental understanding of the corrosion process affecting metals is needed to introduce the topic of "smart coatings" which are engineered to respond to inhibit the effects of corrosive environments. Corrosion is the destructive result of chemical reactions that occur between a metal or a metal alloy and its environment [1, 2]. Corrosion impacts many aspects of our daily lives, and various estimates put the costs to the US economy between 100-300 billion dollars annually. The most striking features of the corrosion process are the immense variety of conditions under which it occurs and the large number of forms in which it appears [3]. Corrosion affects all structural materials and infrastructure of society to cause in many cases grave economic consequences or life-threatening situations. Infrastructure items that can be significantly damaged and eventually destroyed by corrosion include pipelines, bridges, automobiles, storage tanks, airplanes and ships (both military and commercial). The most common environments for corrosion to occur are in natural waters, atmospheric moisture, rain and man-made solutions (such as storage tanks) [4]. The ionic conductivity of an aqueous corrosive environment creates electrochemical reactions [5]. These reactions are strongly influenced by the surface potential and acidity or basicity of the environment which allows electrochemical reactions to take place on a metal surface. This changes the metal from the metallic state to a non-metallic state. The products of corrosion can be dissolved species or solid corrosion products. No matter what the scenario, the energy of the system is lowered as the metal converts to a lower-energy form. The most studied example of this phenomenon is the rusting of iron. The metal (iron) is converted into the corrosion product, the non-metallic form (rust or iron oxides). The difficulty in preventing corrosion from occurring is both a scientific and engineering problem. Corrosion science is the study of the electrochemical processes and metallurgical processes that occur during corrosion in various environments. Corrosion engineering, on the other hand, is the design of methods and materials to prevent corrosion. An understanding of both disciplines is essential to prevent corrosion from affecting infrastructure. There are generally several forms of corrosion that affect infrastructure. These corrosion forms are classified as (i) uniform or general corrosion, (ii) galvanic corrosion, (iii) pitting corrosion, (iv) environmentally-induced cracking, (v) hydrogen damage, (vi) intergranular corrosion, (vii) dealloying and (viii) erosion corrosion [6]. There are several corrosion-preventing barriers: anodic oxides, organic coatings, ceramics, inorganic coatings, phosphate and other conversion coatings [7]. These coatings provide a barrier that resists penetration by aggressive environmental constituents. The goal of these coatings is to prevent the cathodic reaction from taking place beneath the coating (Equation 1).

**Equation 1** $$2\,H_2O + O_2 + 4e^- \rightarrow 4OH^-$$

These coatings work well, but over time the barrier coating can fail due to prolonged exposure to the environment. The organic coatings can develop what is called "under coating corrosion" which initiates from weak spots and develops into blisters and filiform threads leading to corrosion failure [8]. The organic protective coating (barrier coating) fails by separation at the coating/substrate interface [9]. The separation process is known as *delamination*. In time, delamination results in under film corrosion and eventual loss of the barrier properties of the coating. The corrosion-induced delamination occurs as a direct consequence of the electrochemical mechanism of corrosion [5]. The anodic (electron generating) and the cathodic (electron-consuming) reactions occur at the sites where delamination has occurred. The kinetic barriers are, at a minimum, due to the high electrical conductivity of the metal. This provides an easy pathway for electrons between the anodic and cathodic sites. Metal pretreatments have been used to extend the lifetimes of barrier coatings. These pretreatments are normally composed of phosphates, chromates and oxides, which contain a variety of metal cations. These processes are well established industrially and prolong the lifetimes of barrier coatings through better adhesion of the coatings onto the metal substrate. Pretreatments and primers that are used for corrosion protection-specifically Cr(VI) pretreatments such as CCC's and chromate containing primers contain Cr(VI). The Cr(VI) used in CCC and primers is a known human carcinogen [10] and is highly regulated [11]. Alternative approaches are needed to replace barrier coatings that give limited lifetimes for corrosion protection. Ideally, the material should not only provide the benefits of barrier coatings but also passivate the metal, allowing the corrosion current to shift to the noble metal region.

An important component of corrosion inhibition for the protection of metal structures requires that an organic coating release soluble inhibitors into the corrosive environment thereby protecting the exposed metal/alloy. The inhibitor release is usually from a chemical species (pigment) dissolved or dispersed in the coating. Once moisture penetrates the coating, there is a release of these sparingly soluble inorganic compounds through dissolution of the pigment [12]. A well known example of this process is $SrCrO_4$-epoxy primers. These primers release inhibitor ions after dissolution of the pigment. These inhibitors can diffuse and migrate to the coating-metal interface to either passivate the surface or to heal defects in the coating.

### 1.1.2 Corrosion Protection with Smart Coatings and/or Inhibitors

A recent report by the Multidisciplinary University Research Initiative (MURI) Program has identified 2,5-dimercapto-1,3,4-thiadiazole (DMcT) as a corrosion inhibitor comparable to Cr(VI) but without the toxic properties of Cr(VI) [13]. DMcT has been examined as a smart corrosion inhibitor for several decades. There are numerous reports in the literature regarding the ability of DMcT compounds and their derivatives to inhibit corrosion on various metals such as copper-zinc alloys [14], zinc [15], and copper [16].

EAPs such as polyaniline (PANI), polythiophene (PT), polypyrrole (PPy) have been demonstrated to provide corrosion inhibition of various metal substrates by stabilizing the potential of a metal in a passive regime, thereby maintaining a protective oxide layer on the metal [17-20]. A key property of the EAPs is their ability to bind and expel molecules or ions in response to an electrochemical potential [21]. The switching of the EAP redox state can be triggered by a local electrochemical reaction on the surface of

the metal. Dopant ions that act as inhibitors are released upon reduction of the EAP, which can occur during galvanic ion exchange between the oxidizing metal surface and the EAP. Thus, the release of corrosion inhibitors typically will not occur until the corrosion process (metal oxidation) takes place, at which time the inhibitor will diffuse through the coating and will shut down the anodic (or cathodic) corrosion reaction upon encountering the corrosion site. The local galvanic action will then stop, thereby preventing further release of the inhibitor from the EAP (see Figure 1).

As shown in Figure 1 the mechanism depicts a pinhole through a coating on an aluminum alloy (AA 2024-T3) where DMcT is the dopant (D) and the EAP is PANI. The oxygen reduction reaction (ORR) on the cathodic corrosion site initiates corrosion in the adjacent matrix. As aluminum and magnesium leave the surface, copper sponge remains behind. At the same time, DMcT released from the reduced EAP adsorbs onto the copper-rich intermetallic inclusions shutting down the ORR and the subsequent corrosion. This mechanism is called "smart inhibition" and the coating is termed a "smart coating."

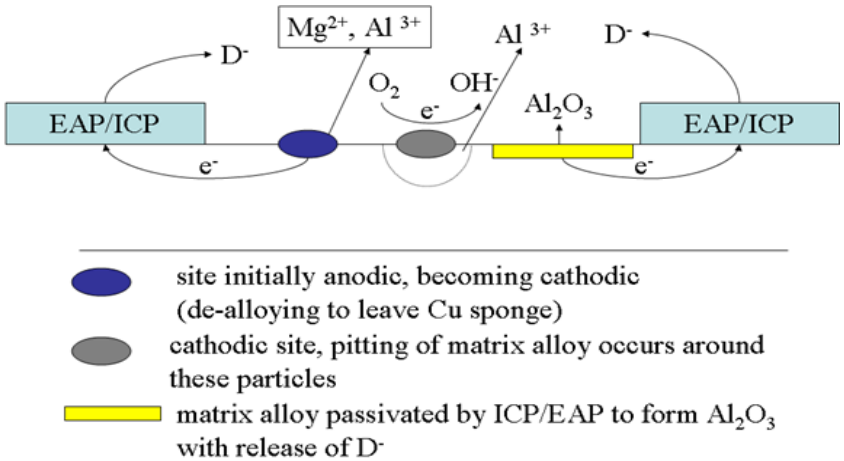



**Figure 1**: DMcT (depicted above as $D^-$) reductively released by corrosion processes on AA 2024-T3

Crosslink has developed a Cr(VI)-free epoxy primer using corrosion-inhibiting compounds (2,5-dimercapto-1,3,4-thiadiazole, DMcT) derivatives that have been demonstrated to mimic the corrosion inhibiting properties of Cr(VI) [22]. Since Cr(VI) has been shown to inhibit corrosion through a release of unreacted and available Cr(VI) when exposed to a corrosive environment, researchers at Crosslink have developed a coating to mimic this process. Cr(VI) protects metal substrates by inhibiting the ORR at a coating defect interface through irreversible electrosorption at sites otherwise catalytic to oxygen reduction. The DMcT inhibitor derivatives that have been developed at Crosslink can replicate this Cr(VI) corrosion inhibition mechanism without the environmental liabilities.

## 1.2 Objective(s) of the Laboratory Studies

The objective(s) of this completed two-year laboratory study project were as follows:

- eliminate (Cr(VI)) from military primer formulations that are currently found on aluminum and steel alloys,
- incorporation of a corrosion-inhibiting compound such as derivatives of 2,5-dimercapto-1,3,4-thiadiazole, (DMcT), which have been shown to mimic the corrosion inhibiting properties of Cr(VI) into epoxy or CP formulations,
- provide the DoD with an attractive Cr(VI)-free alternative,
- test DMcT formulations with Cr(VI) controls for performance by the Navy, Air Force (AF), Army, and industry (Crosslink),
- each co-performer tested the Crosslink Cr(VI)-free primer formulations on military substrates using full coatings under controlled laboratory conditions, and the
- best performing military coating containing the Crosslink DMcT inhibitor was transitioned to ESTCP WP Project # WP-201132.

The above objectives have been met during this two-year laboratory study. Several promising DMcT derivative inhibitor formulations have been prepared, formulated and tested by each co-performer. The tests conducted by each co-performer showed that the Crosslink DMcT inhibitor in certain military coating systems could meet military requirements for alternatives to Cr(VI) primers. However, the Crosslink DMcT primer formulation required a CCC pretreatment with topcoat to compete with the full Cr(VI) military coating. This represents a significant reduction (~ 98%) in the amount of Cr(VI) used in military coating.

By removing almost all Cr(VI) in military primers, this work represents a major improvement in current non-Cr(VI) primer systems. OSHA has published a final standard for occupational exposure to Cr(VI) in the Feb. 28, 2006, Federal Register. The standard covers occupational exposure to Cr(VI) due to the known carcinogenic nature of this compound and it is highly regulated by the EPA and OSHA [11]. OSHA has determined based upon the best scientific evidence, that at the current permissible exposure limit (PEL) for Cr(VI), workers face a significant risk to their health. Therefore, a final rule establishes a permissible exposure limit (PEL) of 25 micrograms of Cr(VI) per cubic meter of air for aerospace painting (25 $\mu g/m^3$) as an 8-hour time weighted average (TWA) for all Cr(VI) compounds in the paint hangar. This ruling was based on extensive consideration of all comments and evidence submitted during this process. However, the PEL for the maintenance worker is still 5$\mu g/m^3$. This standard must be met during painting by using protective personnel equipment (PPE).

## 1.3 Regulatory Drivers

As a result of the new Cr(VI) OSHA regulations as defined in the Feb. 28, 2006, Federal Register, these new standards will now cover occupational exposure to Cr(VI) for workers during an 8-hour TWA period. In order for the DOD to comply with these regulations there will be an increase in disposal costs for Cr(VI) waste paint as a hazardous material. The costs associated for industry/government to comply with the new federal Cr(VI) PEL are summarized in Table 2 [11]. The estimates shown below are considered general costs in complying with the 5 $\mu g/m^3$ requirement air emissions. An alternative Cr(VI)-free primer has been developed by Crosslink. This will allow for easy compliance with OSHA and EPA requirements during painting/repainting operations without any exposure to Cr(VI). This new Crosslink primer formulation would not be considered hazardous materials nor expose workers to hazardous air emissions. The DOD would not be required to comply with expensive disposal costs associated with Cr(VI).

As of January 24, 2013, the National Institute for Occupational Safety and Health (NIOSH) had posted a document entitled "Criteria for a Recommended Standard: Occupational Exposure to Hexavalent Chromium." NIOSH reviewed the critical health effect studies of Cr(VI) compounds and updated its assessment of the potential health effects of occupational exposure to Cr(VI) compounds. The recommendation for the new PEL is 0.20 $\mu g/m^3$ for a workplace environment [11]. This recommendation by NIOSH was advisory only; NIOSH cannot issue a regulatory directive.

The European Union (EU) Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) regulations (EC 1907/2006) were adopted in December 2006, and came into force June 2007. REACH was introduced because many thousands of chemicals are used in the EU, some in very large quantities and with increased risks to human health and to the environment. Cr(VI) is one of the many substances that are highly regulated by the EU and is currently a substance of very high concern (SVHC).

**Table 2**: Estimated Compliance Costs for General Industry with New Cr(VI) Guidelines [11b]

| Cost Category | 10 $\mu g/m^3$ | 5 $\mu g/m^3$ | 1 $\mu g/m^3$ | 0.5 $\mu g/m^3$ | 0.25 $\mu g/m^3$ |
|---|---|---|---|---|---|
| Engineering Controls | $10,652,864 | $14,475,735 | $26,474,262 | $52,467,526 | $82,207,372 |
| Initial Exposure Assessment | $15,250,335 | $15,250,335 | $15,250,335 | $15,250,335 | $15,250,335 |
| Periodic Monitoring | $24,605,517 | $30,034,467 | $60,305,070 | $126,687,514 | $161,729,092 |
| Respirators | $29,448,797 | $29,448,798 | $35,361,768 | $40,773,063 | $56,907,196 |
| Medical Surveillance | $21,211,591 | $13,230,302 | $67,359,536 | $62,126,618 | $79,073,671 |
| Communication of Hazards | $21,211,591 | $21,193,263 | $21,881,436 | $21,889,546 | $21,892,346 |

# 2.0 DEMONSTRATION TECHNOLOGY

## 2.1 Technology Description

This new Crosslink primer formulation can be incorporated into either a Cr(VI)-free epoxy or in a CP formulation. The Crosslink inhibitor was formulated into an epoxy in order to focus the direction of this program and improve success under the guidance of the ESTCP review panel.

Current Cr(VI)-free primer systems have not met the performance requirements of the Cr(VI) military primer systems. By utilizing this new Crosslink Cr(VI)-free inhibitor in an epoxy, one can significantly reduce the amount of Cr(VI) present in military coating systems. The DoD can potentially eliminate Cr(VI) use in full military coatings by using a Cr(VI)-free pretreatment with the Crosslink Cr(VI)-free primer formulation. The laboratory testing included accelerated weathering testing, adhesion (dry and wet tape tests), solvent resistance and GE impact flexibility. All tests included full military coatings consisting of a pretreatment coating (Cr(VI) and Cr(VI)-free) with primer (Cr(VI) and Cr(VI)-free) and topcoat. Each service will test specific metal substrates using their military coatings against the current military requirement for Cr(VI)-free coatings.

This two-year ESTCP project (WP # 200904) focused on process optimization for the pretreatment/Crosslink primer systems. This was accomplished by testing corrosion performance with various surface preparations, solvent reduction and drying experiments. Surface preparation tests determined if surface deoxidation will provide better adhesion and performance than a surface that has been simply cleaned but still maintains a natural oxide layer. Solvent reduction tests will be done to find the minimum amount of VOC-exempt solvents such as 4-chlorobenzotrifluoride (Oxsol-100) which will be needed for spray application using high volume low pressure (HVLP) spray equipment. Drying experiments were done to determine the required drying time under different temperature and humidity conditions. Crosslink in cooperation with its military partners continued to optimize the Cr(VI)-free primer formulation so that it will be compatible to alternative pretreatment coatings (e.g. BAM-PPV, TCP and Alodine 5200/5700) and the different topcoats (ARL-Chemical Agent Resistance Coating (ARL-CARC), MIL-P-53022 and MIL-P-53030, WPAFB-Advanced Performance Topcoat (WPAFB-APC, e.g. MIL-PRF-85285), NAWCAD topcoats, e.g. MIL-PRF-23377N1, MIL-PRF-53030, MIL-PRF-53022 and MIL-PRF-85582N). Accelerated weathering tests included neutral salt spray (NSS), GM9540 and reparability studies. Additional tests included pull-off adhesion (ASTM D-4541), wet and dry adhesion (ASTM D 3359), color, odor and surface appearance of the coating. Selected substrates would include AA 2024-T3, AA 7075-T6 and high strength steel (HSS 4340) and low grade steel substrates. The best performing Crosslink primer coating was selected for transition to ESTCP WP Project # 201132.

## 2.2 Technology Development

NAWCAD funded Crosslink's Cr(VI)-free primer program on pretreated aluminum from FY05-FY07. The results of this 3-year study showed that a Cr(VI)-free epoxy inhibitor system exceeded the minimum military requirement for alternative Cr(VI) primer systems. The military requirement for a new Cr(VI)-free primer coating requires 2000 hours NSS exposure. The Crosslink primer coating system, (primer + pretreatment) exceeded 3000 hours without evidence of blistering, corrosion in the scribe area or delamination. Additional testing showed that this new Cr(VI)-free primer formulation can pass filiform corrosion, adhesion and fluid resistance testing. The corrosion and mechanical performance data indicate that the Cr(VI)-free inhibitors in the epoxy primer are a potential replacement for military Cr(VI) primer coatings.

"Smart" coating systems are engineered to respond to electrochemical processes responsible for corrosion by providing a self-repairing system. When corrosion events are sensed, the coating functions to automatically release anodic and/or cathodic corrosion inhibitors to shut down the corrosion process. Several smart coating system strategies employ conductive polymers (CPs) or also referred to as inherently conductive polymers (ICPs) such as PANI. These coating systems capitalize on the two unique properties of CPs: a). conduct electricity and b). bind and expel molecules or ions in response to an electrochemical potential. For a smart coating system, the switching of the CP redox state is triggered by local electrochemical reactions occurring on the surface of a metal which occur during a corrosion process. Thus, if the CP is engineered to contain an inhibitor ion as a dopant, the ion is released when a corrosion process (metal oxidation) occurs.

CPs was used by Crosslink containing smart inhibitors based on DMcT in the primer to provide corrosion protection on AA 2024-T3. These aluminum alloys are of great interest in the aerospace industry. In contrast to pure aluminum, which is resistant to pitting corrosion, the increased susceptibility of the AA 2024-T3 aluminum alloy to pitting corrosion is centered upon the unique electrochemistry of the intermetallic inclusions, specifically the oxygen reduction reaction (ORR). Crosslink's early work demonstrated that you can incorporate organic ORR inhibitors into PANI coating systems that are released upon demand. The synthesis, formulation, electrochemical characterization and performance of 2,5-dimercapto-1,3,4-thiadiazole (DMcT) as a dopant for PANI have been accomplished under previous programs. DMcT is a known ORR inhibitor for copper. DMcT is unique in that poly(DMcT) and DMcT form a reversible polymerization-depolymerization redox couple with DMcT being released when poly(DMcT) is reduced. Poly(DMcT) is an electroactive polymer (EAP) as is PANI, but it is not a CP since it is not an electrically conductive polymer. This exclusive property allows for efficient storage of DMcT in its polymeric form. The PANI-DMcT is a heterogeneous polymer blend of PANI and poly(DMcT).

Cyclic Voltammetry (CV) on solutions of aniline and of DMcT with an equivalent of NaOH, both in 0.1 M NaCl, showed simultaneous polymerization of aniline and DMcT. Both DMcT and aniline oxidize at approximately the same potential (+300 mV vs. Ag/AgCl). PANI is reduced at ~ 100 mV in contrast to poly(DMcT) which is reduced at ~ -300 mV vs. AgCl. Figure 2 shows the CV of 10 mM DMcT with 0, 1 and 2 equivalents of NaOH. Since, in the neutral form, DMcT is only slightly soluble in water, only a small oxidation current is detected at 300 mV. Upon addition of 1 equivalent of

hydroxide, one of the –SH groups is deprotonated and the solubility is increased leading to an increase in oxidation current. Upon addition of 2 equivalents of hydroxide, both –SH groups are deprotonated and DMcT is completely solubilized. At about -300 mV vs. AgCl the reduction peak for poly(DMcT) is observed and poly(DMcT) is reductively de-polymerized releasing DMcT.

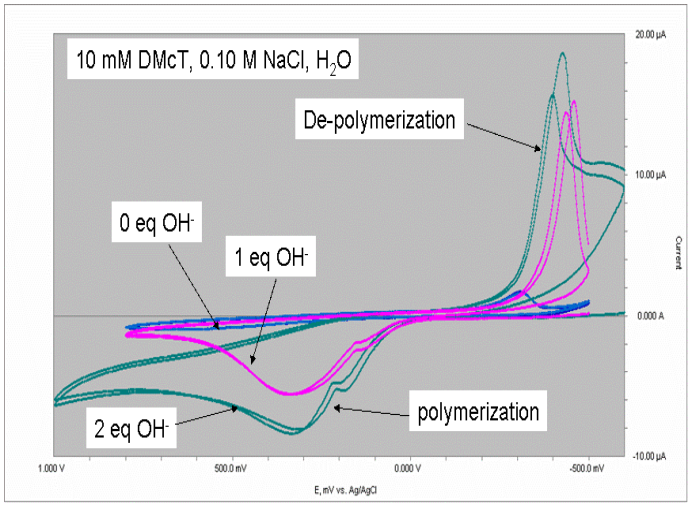



**Figure 2**: Cyclic Voltammetry of DMcT. Scan rate = 20 mV/s

As shown in Figure 3, DMcT is released both by reduction of PANI-DMcT as well as poly(DMcT). Thus at the corrosion potential of AA 2024-T3 in aqueous NaCl, -0.4 to -0.5 V vs. Ag/AgCl, one expects electrochemically driven dopant release.

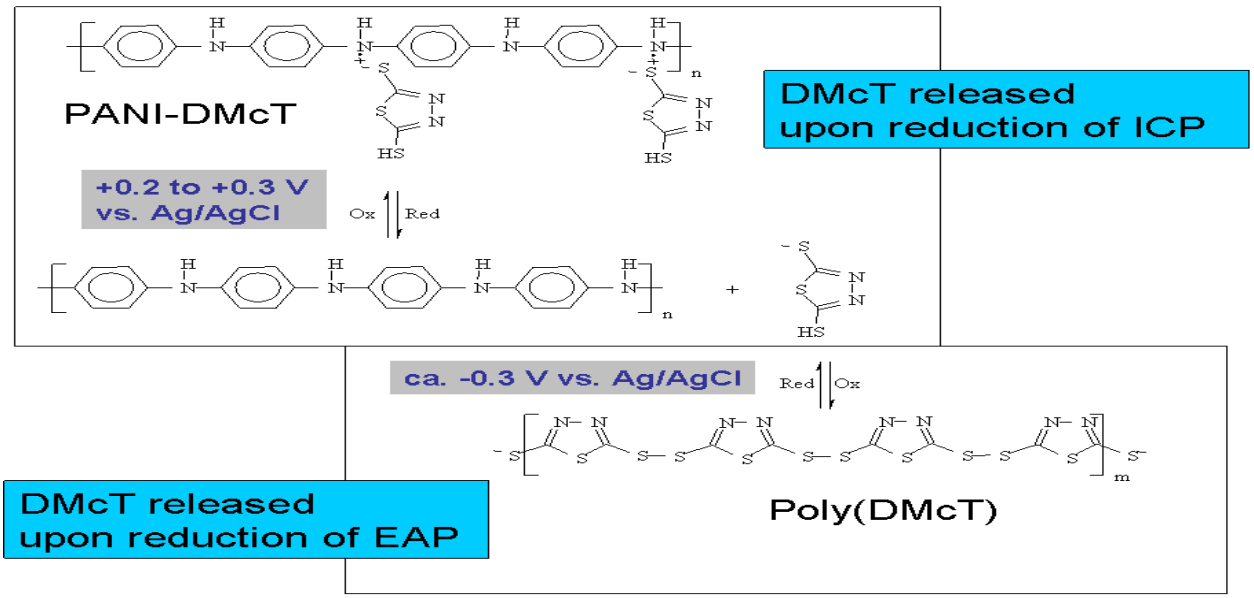
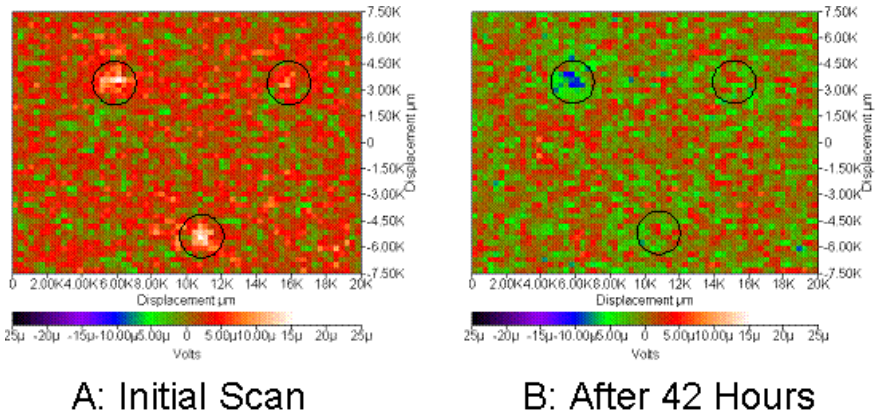



**Figure 3**: DMcT release scheme

Scanning vibrating electrode technique (SVET) was also used to demonstrate the effectiveness of DMcT as a smart corrosion inhibitor. A Pourbaix diagram for aluminum shows that thermodynamically active corrosion was expected at pH < 3 and pH > 8, with a passive aluminum oxide forming between pH 3 and 8. SVET was employed to monitor corrosion in artificially created pinholes in a PANI-DMcT UV-cured coating on AA 2024-T3 immersed in tap water (pH = 8). Aluminum was expected to be actively corroding at this pH. Initially all three pin holes showed cathodic activity as is shown in Figure 4A. After one hour of exposure, no corrosion activity was observed, indicating the cathode reaction has been inhibited as expected. After 42 hours exposure, however, anodic activity was observed to occur as shown in Figure 4B. Thus, although the ORR in the pin holes has been eliminated, anodic galvanic processes are not completely eliminated, as might be expected since DMcT is an ORR inhibitor on copper.




**Figures 4A and 4B**: SVET scan of UV cured PANI-DMcT/poly(DMcT) formulation. Circles depict pin holes (anodic areas are positive volts, cathodic negative)

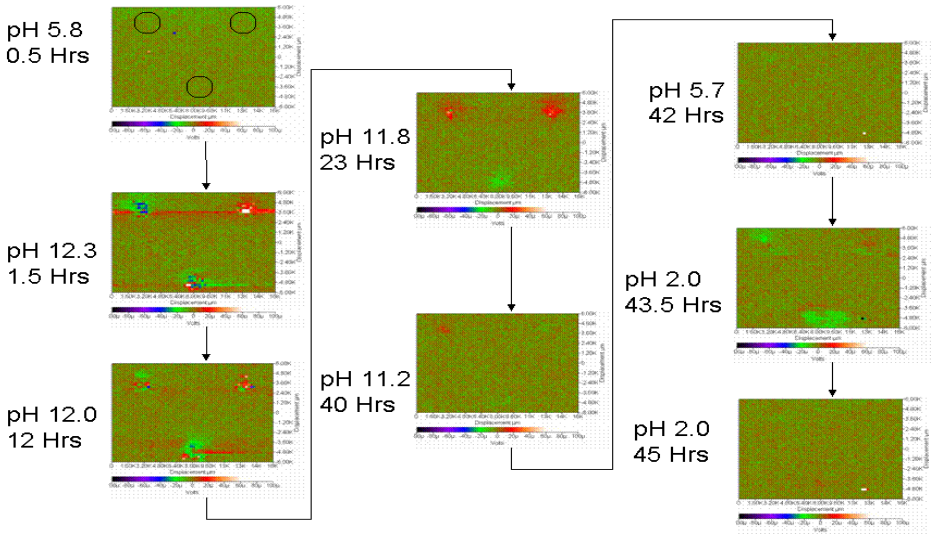



**Figure 5**: SVET scans of PANI-DMcT coated on AA 2024T-3

Figure 5 shows SVET results of PANI-DMcT coating on AA 2024-T3 in 0.01 M NaCl as a function of pH. Initially, at pH 5.6 no corrosion activity is observed. When the pH was raised to 12.3, corrosion activity was detected; however, after 38.5 hours (40 hours into the test) the corrosion activity was undetectable. When the pH was lowered to 2.0 (43.5 hours into the test) activity was detected. However, after an additional 1.5 hours (45 hours into the test) no corrosion activity was detected. These results clearly show corrosion was effectively shut down within hours of initiation under both acidic and basic conditions using the DMcT inhibitor system. Crosslink has demonstrated that oxidative polymerization of aniline and DMcT yields a mixture of both PANI-DMcT and poly(DMcT). When the PANI-DMcT/poly(DMcT) mixture was incorporated into a UV curable coating system, SVET analysis shows corrosion is inhibited on AA 2024-T3. Further testing (Crosslink primer only) on AA 2024-T3 coupons in neutral salt spray (NSS) showed good corrosion inhibition up to 2000 hours of exposure (see Figure 6).

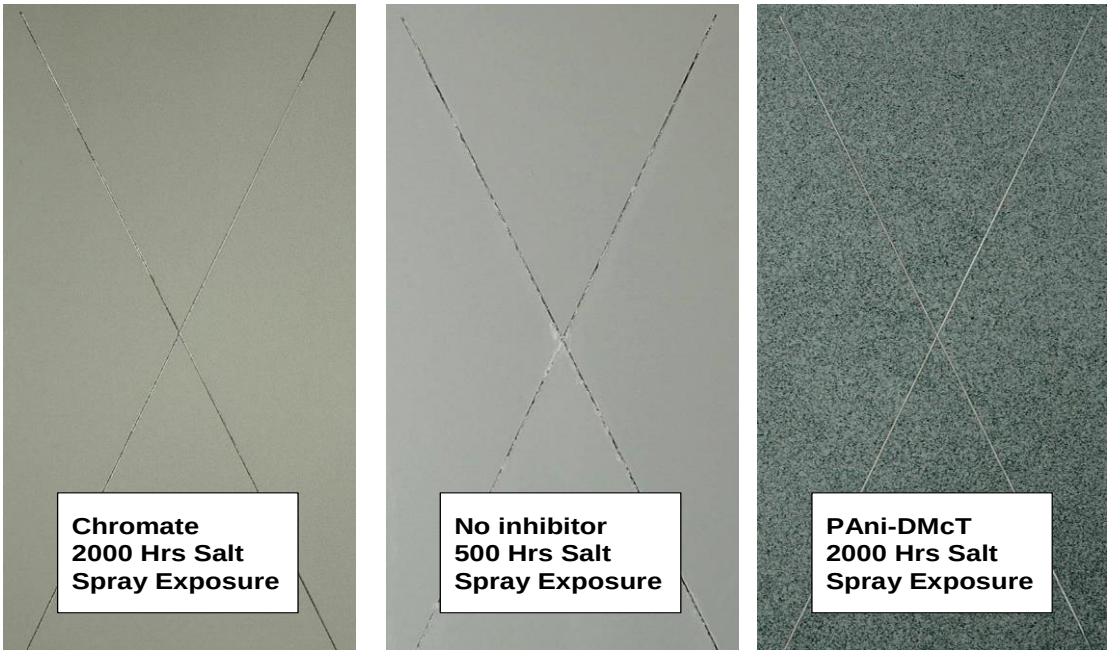



**Figure 6**: Comparison of representative 2k epoxy formulations after ASTM B117 neutral salt fog spray exposure

## 2.3 Advantages and Limitations of the Technology

The expected benefit to the DOD is twofold: a) robust, environmentally benign, repairable Cr(VI)-free primer coating system and b) a significant cost saving in life cycle costs as well as compliance with existing and future environmental regulations. Costs associated with disposal of Cr(VI), health monitoring, record keeping and personal protective equipment (PPE) will be greatly reduced. All O-level, I-level and depot-level maintenance facilities, DOD-wide, should be able to implement this technology with little or no hardware procurement because standard spray and touch-up equipment can be

used. Investment costs will be negligible consisting of only the cost of the new material. Scale-up of the Crosslink primer through a joint venture between Crosslink and a commercial pigment company (Wayne Pigments) has been successfully completed under this ESTCP program.

Not only will there be a cost savings in waste management, but also an immeasurable human and environmental health benefit. The cost reduction associated with disposal and health monitoring of Cr(VI) waste would amount to millions of dollars per year in costs savings. These saving would be due to complying with the new Cr(VI) guidelines. The costs associated with health monitoring, medical surveillance, exposure assessment for Cr(VI) would be eliminated using this proposed technology. The only limitations that this technology could have would be in matching the long term corrosion inhibition of Cr(VI) primers. Currently Cr(VI) primers can exceed 6000 hours NSS exposure and provide continuous corrosion protection. The Crosslink primer while having met minimum DOD requirements must still meet the long term corrosion inhibition of Cr(VI) primers in full military coatings.

## 2.4 PERFORMANCE OBJECTIVES

A Joint Test Protocol (JTP) for "Validation of Non-Hexavalent Chromium (Cr(VI)) Primers/Paint on Aluminum/Steel Coupons Weapons Platforms Project Number 200904," was developed for this program and accepted by the ESTCP Program office July 2010 [23]. This JTP was used at the reference guide for all testing performed on the Crosslink primer systems. Quantitative and qualitative data was collected and used to evaluate the Crosslink primer coating system's ability to replace the Cr(VI) primers, corrosion/adhesion performance, as well as to identify environmental benefits, cost savings, and improvements to mission readiness. Several key performance objectives for this ESTCP WP 200904 project are included in Table 3. The acceptance/rejection criteria for these performance objectives are described in the table.

**Table 3**: Performance Objectives for ESTCP Program WP 200904

| Type of Performance Objective | Primary Performance Criteria | Expected Performance (Metric) | Actual Performance Objective Met? |
|---|---|---|---|
| (1) Eliminate Cr(VI) in Primer coating/ Quantitative | Corrosion Resistance: NSS on Scribed surface | 2000 hours NSS exposure without evidence of blistering, corrosion or delamination | YES meet 2000 hours NSS exposure |
| (2) Adhesion (Crosshatch and wet)/Qualitative | Dry and wet tape adhesion | Must have rating or 4B and 4A to pass | PASS with ratings of 4A and 4B |
| (3) Physical Requirement: Surface Appearance/ Qualitative | Surface smooth, free from runs, sags or bubbles | Must have no defects on the surface | PASS no surface defects on any Crosslink primers |
| (4) Physical Requirement: Odor/Qualitative | Presence of odor after primer application | No odor detected after application | PASS no odor detected on Crosslink primers |
| (5) Physical Requirement: Drying Time/ Qualitative | Tape application without any loss of adhesion in 8 hours or less | No loss of adhesion | PASS no loss of adhesion on any Crosslink primers |
| (6) Filiform/Quantitative | Filiform Corrosion Resistance | All filaments <1/4", Majority <1/8" | FAIL All Crosslink primer coated coupons |
| (7) $SO_2$ Corrosion/ Quantitative | SO2 salt spray exposure on scribed coated primer coupons | 500 hours with no evidence of corrosion (minor surface corrosion in scribe permissible) | FAIL All Crosslink primer coated coupons |
| (8) Cyclic Corrosion Resistance/ Quantitative | Cyclic Corrosion test on scribed coated primer coupons | Equivalent or improved performance compared to Cr(VI) controls | FAIL All Crosslink primer coupons |

# 3.0 TEST DESIGN

During this two-year laboratory study, experiments by each of the co-performers were carried out to determine the corrosion, adhesion, reparability properties of the Crosslink primer. The best performing military coating systems using the Crosslink primer were down selected for transition to the current ESTCP WP Project # 201132.

## 3.1 Laboratory Testing

A JTP was developed for this ESTCP program. This JTP developed by NAWCWD was used as a guide during the two-year laboratory study for this ESTCP project. The following sections describe the laboratory tests performed by each of the co-performers to evaluate the Crosslink primer with various pretreatments and topcoat coatings.

### 3.1.1 Adhesion Testing Methods

#### 3.1.1.2 Crosshatch Adhesion (MIL-PRF-23377)

Crosshatch adhesion testing was performed to determine the adhesion between the substrate, pretreatment, primer, and topcoat interfaces [24]. This test was performed on (*i*) pretreated, (*ii*) primed and (*iii*) topcoated systems for AA 2024-T3 aluminum and 4130 normalized steel substrates. UDRI/CTIO Laboratory Procedure CLG-LP-008, *Tape Test Adhesion*, in accordance with ASTM D 3359, *Standard Test Methods for Measuring Adhesion by Tape Test*, was used for guidance to run the test. Guidance for sample evaluation was taken from MIL-DTL-81706, MIL-PRF-23377, and MIL-PRF-85285, *Performance Specification, Coating: Polyurethane, Aircraft and Support Equipment*. Samples with pretreatment and primer only (no topcoat) were tested using the 1-millimeter spacing crosshatch blade. Topcoated samples were tested with the 2-millimeter spacing crosshatch blade. There were three replicates for each coating system on aluminum samples and one test performed per sample. However, because of limited materials, steel samples only had two replicates per coating system, so there were two tests performed per sample for a total of four readings on each coating system on steel. The ratings provide only general information concerning the overall adhesion performance of the system. The description of the rating scale, as taken from ASTM D 3359, is given in Figure 7 and the visual standard is given in Figure 8.

| | |
|---|---|
| 5B | The edges of the cuts are completely smooth; none of the squares of the lattice is detached. |
| 4B | Small flakes of the coating are detached at intersections; less than 5 % of the area is affected. |
| 3B | Small flakes of the coating are detached along edges and at intersections of cuts. The area affected is 5 to 15 % of the lattice. |
| 2B | The coating has flaked along the edges and on parts of the squares. The area affected is 15 to 35 % of the lattice. |
| 1B | The coating has flaked along the edges of cuts in large ribbons and whole squares have detached. The area affected is 35 to 65 % of the lattice. |
| 0B | Flaking and detachment worse than Grade 1. |

**Figure 7**: ASTM D 3359, Method B, Crosshatch Adhesion Rating Scale Description

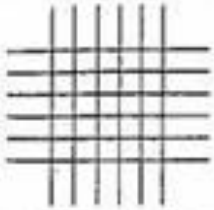
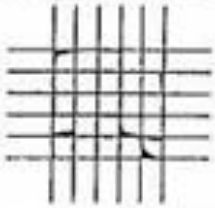
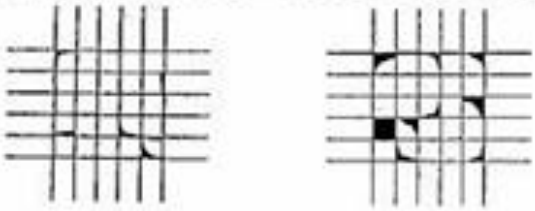
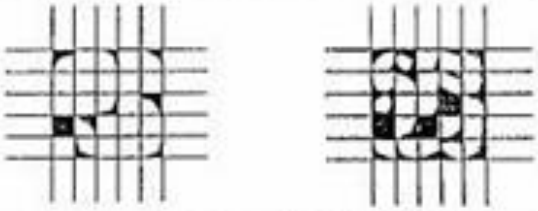
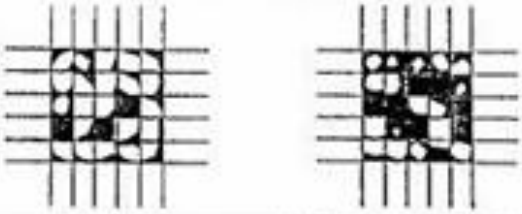
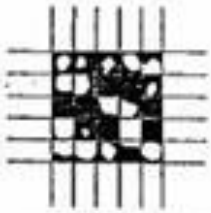
| CLASSIFICATION OF ADHESION TEST RESULTS | | |
|---|---|---|
| CLASSIFICATION | PERCENT AREA REMOVED | SURFACE OF CROSS-CUT AREA FROM WHICH FLAKING HAS OCCURRED FOR SIX PARALLEL CUTS AND ADHESION RANGE BY PERCENT |
| 5B | 0% None |  |
| 4B | Less than 5% |  |
| 3B | 5 - 15% |  |
| 2B | 15 - 35% |  |
| 1B | 35 - 65% |  |
| 0B | Greater than 65% |  |

**Figure 8**: ASTM D 3359, Method B, Crosshatch Adhesion Visual Standard Reference Image

#### 3.1.1.3 X-Cut Tape Adhesion (MIL-PRF-85285)

X-cut tape adhesion testing was performed according to ASTM D 3359, Method A, to determine the adhesion between the substrate, pretreatment, primer, and topcoat interfaces when the coating is greater than 5 thousandths of an inch in thickness [25]. This test was performed on reparability samples (sized 12 x 12 inches) following 2000 hours of total UVB exposure. UDRI/CTIO Laboratory Procedure CLG-LP-008 was used for guidance to run the test and to evaluate the samples. There were three replicates for each coating system, and two tests were performed per sample; one on the right side of the panel and one of the left side.

#### 3.1.1.4 Wet-Tape Adhesion (MIL-PRF-23377, MIL-PRF-85285)

The wet-tape adhesion test is specified in MIL-PRF-23377 and MIL-PRF-85285. It is designed to measure inter-coat adhesion of an organic coating immersed in water for a short period of time. This test was performed on (*i*) primed and (*ii*) topcoated systems for AA 2024-T3 substrates only. UDRI/CTIO Laboratory Procedure CLG-LP-033, Wet Tape Adhesion, conformed to Federal Test Method Standard (FTMS) 141D, *Paint, Varnish, Lacquer and Related Materials: Methods of Inspection, Sampling, and Testing*, Method 6301, *Adhesion (Wet) Tape Test*, These methods were used for guidance to run the test and to evaluate the samples (see Table 4). There were three replicates per coating system.

**Table 4**: ASTM D 3359 Adhesion, Method A, Rating Scale

| | |
|---|---|
| 5A | No peeling or removal of coating |
| 4A | Trace peeling or removal along incisions or intersections |
| 3A | Jagged removal along incisions up to 1/16 inch on either side |
| 2A | Jagged removal along most of incisions up to 1/8 inch |
| 1A | Removal from most of the inscribed area |
| 0A | Removal beyond the inscribed area |

#### 3.1.1.5 Pull-Off Adhesion ASTM D 4541 PATTI:

The pneumatic adhesion tensile test instrument (PATTI) pull-off test is designed to give specific information concerning both the inter-coat adhesion and the intra-coat cohesion of organic coating systems [26]. This test was performed on (*i*) primed and (*ii*) topcoated systems for AA 2024-T3 substrates only. UDRI/CTIO Laboratory Procedure CLG-LP-046, Tensile Adhesion, in accordance with ASTM D 4541, *Standard Test Method for Pull-Off Strength of Coatings Using Portable Adhesion Testers*, was used for guidance to run the test and to evaluate the samples. This test is defined by ASTM as a measure of the direct normal applied force required to remove one or more layers from a coating system as a measure of adhesion strength. The raw data are the psi-gauge values from the apparatus, and these values were converted to direct pull-off tensile strength (psi) using the following equation (Equation 2).

**Equation 2** pull-off tensile strength (psi) = [(ab)-c]/d

Where;

a = contact area of the gasket in the F-8 piston = 8in$^2$
b = burst pressure from gauge (psig)
c = piston constant for F-8 = 1.068 lbs
d = contact area of the pull stub = 0.196 in$^2$

There are limitations to interpretation of the data that was generated from these studies. Those limitations can be summarized from the scope of the method as defined by ASTM and quoted here "1.0 Scope 1.1. This test method covers a procedure for evaluating the pull-off strength (commonly referred to as adhesion) of a coating on rigid substrates such as metal, concrete or wood. The test determines either the greatest perpendicular force (in tension) that a surface area can bear before a plug of material is detached, or whether the surface remains intact at a prescribed force (pass/fail). Failure will occur along the weakest plane within the system comprised of the test fixture, adhesive, coating system, and substrate, and will be exposed by the fracture surface. This test method maximizes tensile stress as compared to the shear stress applied by other methods, such as scratch or knife adhesion, and results may not be comparable." The following criteria were applied to the data to determine outliers, suspect data, and confidence intervals. ASTM recommends that a statistical analysis for outliers is performed on all data sets to reject unreliable numerical pull-off values. Although the data are numerical and quantitative, the failure modes are qualitative. Therefore, ASTM recommends that the numerical value for the pull-off be disregarded when more than 50% of the failure mode was the result of adhesive failure. Final guidance on the interpretation of the data is given concerning the precision data, which is instrument and laboratory dependent. The instrument used for this test was the Type IV self-alignment adhesion tester as defined in ASTM D 4541. The precision of this test method, as defined by ASTM, is that three replicates of any test specimen must not differ by more than 29% to provide a confidence interval of 95% for that data.

Samples were milled with a 0.5 inch inner-diameter ring prior to testing. Samples were cleaned with methanol prior to pull-stub application rather than more aggressive solvents, to prevent adverse effects to the electroactive polymer prior to testing. Light abrasion with 240-grit sandpaper was used on primed and topcoated samples. There were three samples from each coating system, and those samples were cut in half to produce a total of 6 replicates per coating system for this test. The reported data are numeric and are the result of the calculated pull-off strength of either the coating layers that are removed or the maximum of the adhesive. For coating systems with multiple coatings (i.e., primer followed by topcoat), a description of the nature of the coating failure is included with the reported numerical value of the pull-off. A guideline to those descriptions is given in Table 5.

| **Table 5**: PATTI Coating Failure Descriptions | | |
|---|---|---|
| **Notation** | **Description** | **Failure Mode** |
| T/T | Topcoat on pull stub and panel surface | Topcoat–Topcoat Cohesion |
| T/P | Topcoat on pull stub and primer on panel surface | Topcoat–Primer Adhesion |
| P/P | Primer on pull stub and on panel surface | Primer–Primer Cohesion |
| P/S | Primer on pull stub and no visible coating on panel surface (includes failures at the conversion coating, if visible) | Primer–Substrate Adhesion |
| T/E | Topcoat on panel and epoxy either on panel or on stub (Epoxy failure only – no coating failure noted) | Topcoat–Epoxy Adhesion |
| P/E | Primer on panel and epoxy either on panel or on stub (Epoxy failure only – no coating failure noted) | Primer–Epoxy Adhesion |
| tension that a primer surface area can bear and remains intact / Pretreat | Primer on the stub and pretreatment on the panel (Specific reference to BAM-PPV which is readily visible) | Primer–Pretreatment Adhesion |
| Pretreat / Pretreat | Pretreatment on the stub and on the panel (Specific reference to BAM-PPV which is readily visible) | Pretreatment–Pretreatment Cohesion |

Pull-off adhesion testing of BAM-PPV coatings by ARL was measured to assess the effects of pretreatment or surface preparation at the substrate. These tests were performed in accordance with ASTM D 4541. An Elcometer Model 108 Hydraulic Adhesion Test Equipment (HATE) (Figure 9) was used for this procedure. In addition to being a more quantitative test method, pull-off adhesion is also less prone to human elements in testing such as variations in pressure applied during scribing as well as interpretation and perception of results. For the pull-off adhesion test, a loading fixture commonly referred to as a "dolly" is secured normal to the coating surface using an adhesive. The adhesive used was cyanoacrylate. After allowing the adhesive to cure for 24 hours at 25$^{o}$C in ambient conditions, the attached dolly was inserted into the test apparatus. The load applied by the apparatus was gradually increased and monitored on the gauge until a plug of coating was detached. The failure value (in psi) was recorded and the failure mode was characterized. For pull-off data to be valid, the specimen substrate must be of sufficient thickness to ensure that the coaxial load applied during the removal stage does not distort the substrate material and cause a bulging or "trampoline effect." When a thin specimen is used, the resultant bulge causes the coating to radically peel away outwards from the center instead of being uniformly pulled away in pure tension and thus results in significantly lower readings than for identically prepared specimens with greater substrate thickness. At 0.25 inches, all of the metallic panels evaluated in the test matrix had adequate thickness for valid pull-off test results. Measurements for each coating system and substrate were obtained by taking 16 measurements on each of the two panels within each set for a total of 32 replicates. Any failure measurements due to coating separation between the topcoat surface and the cyanoacrylate adhesive were rejected.

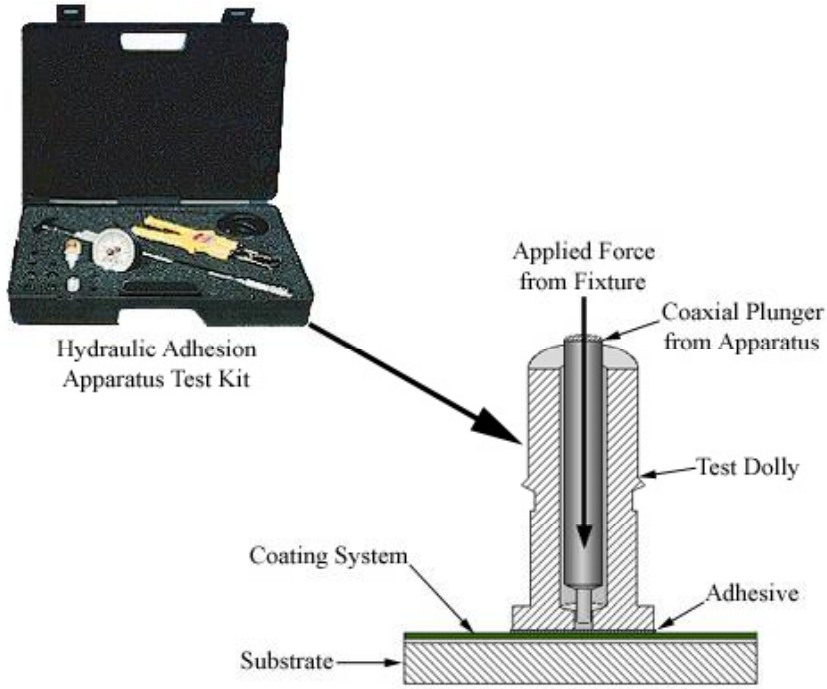



**Figure 9**: Hydraulic Adhesion Test Equipment and Dolly configuration

### 3.1.2 Accelerated Weathering Tests

#### 3.1.2.1 Neutral Salt Spray Exposure (MIL-DTL-81706, MIL-PRF-23377)

Neutral salt spray (NSS) exposure testing was performed to evaluate the ability of the coating systems to withstand a 5-weight percent sodium chloride solution, pH-adjusted to a range of 6.5 – 7.2 [26]. This test was performed on

- pretreatment,
- primed, and
- topcoated systems on AA 2024-T3 aluminum substrates.

UDRI/CTIO Laboratory Procedure CLG-LP-019, *Salt Fog Corrosion*, in accordance with ASTM B 117, *Standard Practice for Operating Salt Spray (Fog) Apparatus*, was used for guidance to run the test. All samples subject to salt spray exposure were photographed before and after the test to document the coating performance. There were three replicates per coating system. The guidance for sample evaluation was taken from MIL-DTL-81706, *Chemical Conversion Materials for Coating Aluminum and Aluminum Alloys*, and MIL-PRF-23377, P*erformance Specification, Primer Coatings: Epoxy, High Solids*. Samples that were pretreated-only were exposed for 336 hours and checked for blistering or signs of corrosion. Discoloration was not cause to reject pretreatment-only samples. Samples that were primed or primed and topcoated were scribed with an X-scribe (full size), exposed for 2000 hours, and checked for blistering, loss of adhesion, undercutting, pitting, and corrosion build-up in the scribe.

The rating systems for primed and topcoated samples exposed to neutral salt spray are given in Tables 6-8 and are derived from ASTM methods and historical practices for military specification interpretations. **The AF has used these rating systems based on a comparative scale for corrosion data. Specifically WPAFB Logistics Systems Support Branch Office (RXSSO) has used this rating system for decades due to its easy interpretation and uniformity. This reporting has been followed by additional laboratories to make presentation and interpretation of data more easily understood by non-corrosion scientists and engineers. The rating numbers are referenced in this order:**

- **1st number = appearance,**
- **2nd number = undercutting and**
- **3rd number = blistering.**

Ratings are listed along with an interpretation rating of "acceptable", "low", or "poor". An interpretation rating of "acceptable" is minor corrosion no greater than 2. An interpretation rating of "low" is minor corrosion no greater than 2 in combination with undercutting no greater than 1 or blistering equal to 1. An interpretation rating of "poor" is any combination of ratings for corrosion, undercutting, or blistering that is greater than the previous two mentioned. For example, a rating of 2 0 0 is considered "acceptable" performance and is comparable to control data. A rating of 2 0 1 is considered "low" performance because it is slightly less robust than the control data. A rating of 2 3 0 or 2 2 1 is considered "poor" performance because it is much less robust than the control data and does not provide comparable performance.

**Table 6**: RXSSO Scribe Appearance Rating System

| Rating | Evaluation |
|---|---|
| 0 | Bright and clean |
| 1 | Staining no corrosion build up |
| 2 | Minor corrosion build up |
| 3 | Moderate corrosion build up |
| 4 | Major corrosion build up |
| 5 | Severe corrosion buildup |

**Table 7**: RXSSO Undercutting Rating System

| Rating | Evaluation |
|---|---|
| 0 | No lifting of coating |
| 1 | Lifting or loss of adhesion up to 1/16 in. (2 mm) |
| 2 | Lifting or loss of adhesion up to 1/8 in. (3 mm) |
| 3 | Lifting or loss of adhesion up to 1/4 in. (6 mm) |
| 4 | Lifting or loss of adhesion up to 1/2 in. (13 mm) |
| 5 | Lifting or loss of adhesion beyond 1/2 in. (>13 mm) |

**Table 8**: Blistering Rating System (Modified from ASTM D 714)

| Blister Size | | | Blister Frequency | |
|---|---|---|---|---|
| **ASTM D 714 Rating** | **CTIO Rating Scale** | **Evaluation** | **Rating** | **Evaluation** |
| 10 | 0 | None | F | Few |
| 8 | 1 | Very small | M | Medium |
| 6 | 2 | Small | MD | Medium Dense |
| 4 | 3 | Medium | D | Dense |
| 2 | 4 | Large | | |
| 0 | 5 | Delamination | | |

### 3.1.2.2 Accelerated Corrosion Test (GM9540P)

GM9540P is an accelerated corrosion test developed by General Motors that was designed for the evaluation of assemblies and components [27]. Steel substrates often perform poorly when scribed and placed in ASTM B 117 salt spray exposure because of the nature of that accelerated test. Because the GM9540P, *Accelerated Corrosion Test*, was designed for steel substrates, this test has provided good results for the anticipated corrosion behavior of organic coating systems. Typically, accelerated corrosion test performance is not rated by the brightness of the scribe or the character of the scribe corrosion since only a very small amount of $Fe_2O_3$ and FeOOH is necessary to generate visible discoloration which often leads to erroneous "fail" ratings. For these systems, sample corrosion was rated based upon SSPC/NACE guidelines which recommend ASTM D 1654, *Standard Test Method for Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments*, for corrosion undercutting at the scribe, ASTM D 610, *Standard Test Method for Evaluating Degree of Rusting on Painted Steel Surfaces*, for corrosion of steel in the field of the sample, and ASTM D 714, *Standard Test Method for Evaluating Degree of Blistering of Paints*, for blistering in the field of the sample. This test was performed on (*i*) primed and (*ii*) topcoated systems for 4130 normalized (4130N) steel substrates only. Half of the samples were grit-blasted with 120-grit aluminum oxide prior to application of the pretreatment, and the other half of the samples were solvent-cleaned with a combination of mineral spirits wipes, Brulin 815GD detergent cleaner immersion, and methyl ethyl ketone wipes to remove surface debris

prior to application of the pretreatment (no abrasive cleaning). This provided two substrate systems denoted with "grit-blasted" and "solvent-cleaned." One representative sample from each coating system was photographed at the initial point, prior to exposure to GM9540P for reference. Primed and topcoated samples received a single scribe line down the center of the panel (not an "X"), and were exposed for 40 cycles (5 cycles per week, with samples left untouched over weekends). One representative sample from each coating system was photographed at the beginning of the test, weekly for the duration of the test, and at the end of the test. There were three replicates per coating system. For these systems, sample corrosion was rated based upon SSPC/NACE guidelines which recommend ASTM D 1654, *Standard Test Method for Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments*, for corrosion undercutting at the scribe, ASTM D 610, *Standard Test Method for Evaluating Degree of Rusting on Painted Steel Surfaces*, for corrosion of steel in the field of the sample, and ASTM D 714, *Standard Test Method for Evaluating Degree of Blistering of Paints*, for blistering in the field of the sample. The rating scales for these ASTM standards are given in Tables 9 and 10 and Figure 10.

**Table 9**: Rating of Failure at Scribe (Procedure A)
Representative Mean Creepage from Scribe

| Millimeters | Inches (approximate) | Rating Number |
|---|---|---|
| Zero | 0 | 10 |
| Over 0. to 0.5 | 0 to $\frac{1}{64}$ | 9 |
| Over 0.5 to 1.0 | $\frac{1}{64}$ to $\frac{1}{32}$ | 8 |
| Over 1.0 to 2.0 | $\frac{1}{32}$ to $\frac{1}{16}$ | 7 |
| Over 2.0 to 3.0 | $\frac{1}{16}$ to $\frac{1}{8}$ | 6 |
| Over 3.0 to 5.0 | $\frac{1}{8}$ to $\frac{3}{16}$ | 5 |
| Over 5.0 to 7.0 | $\frac{3}{16}$ to $\frac{1}{4}$ | 4 |
| Over 7.0 to 10.0 | $\frac{1}{4}$ to $\frac{3}{8}$ | 3 |
| Over 10.0 to 13.0 | $\frac{3}{8}$ to $\frac{1}{2}$ | 2 |
| Over 13.0 to 16.0 | $\frac{1}{2}$ to $\frac{5}{8}$ | 1 |
| Over 16.0 to more | $\frac{5}{8}$ to more | 0 |

**Table 10**: Rating Scale from ASTM D 610

| Rust Grade | Percent (%) of Surface Rusted | Spots (S) (Visual) | General (G) (Visual) | Pinpoint (P) (Visual) |
|---|---|---|---|---|
| 10 | Less than or equal to 0.01 % | | None | |
| 9 | Greater than 0.01 % and up to 0.03 % | 9-S | 9-G | 9-P |
| 8 | Greater than 0.03 % and up to 0.1% | 8-S | 8-G | 8-P |
| 7 | Greater than 0.1% and up to 0.3% | 7-S | 7-G | 7-P |
| 6 | Greater than 0.3% and up to 1.0% | 6-S | 6-G | 6-P |
| 5 | Greater than 1.0% and up to 3.0% | 5-S | 5-G | 5-P |
| 4 | Greater than 3.0% and up to 10.0% | 4-S | 4-G | 4-P |
| 3 | Greater than 10.0% and up to 16.0 % | 3-S | 3-G | 3-P |
| 2 | Greater than 16.0% and up to 33.0% | 2-S | 2-G | 2-P |
| 1 | Greater than 33.0% and up to 50.0% | 1-S | 1-G | 1-P |
| 0 | Greater than 50.0% | | None | |

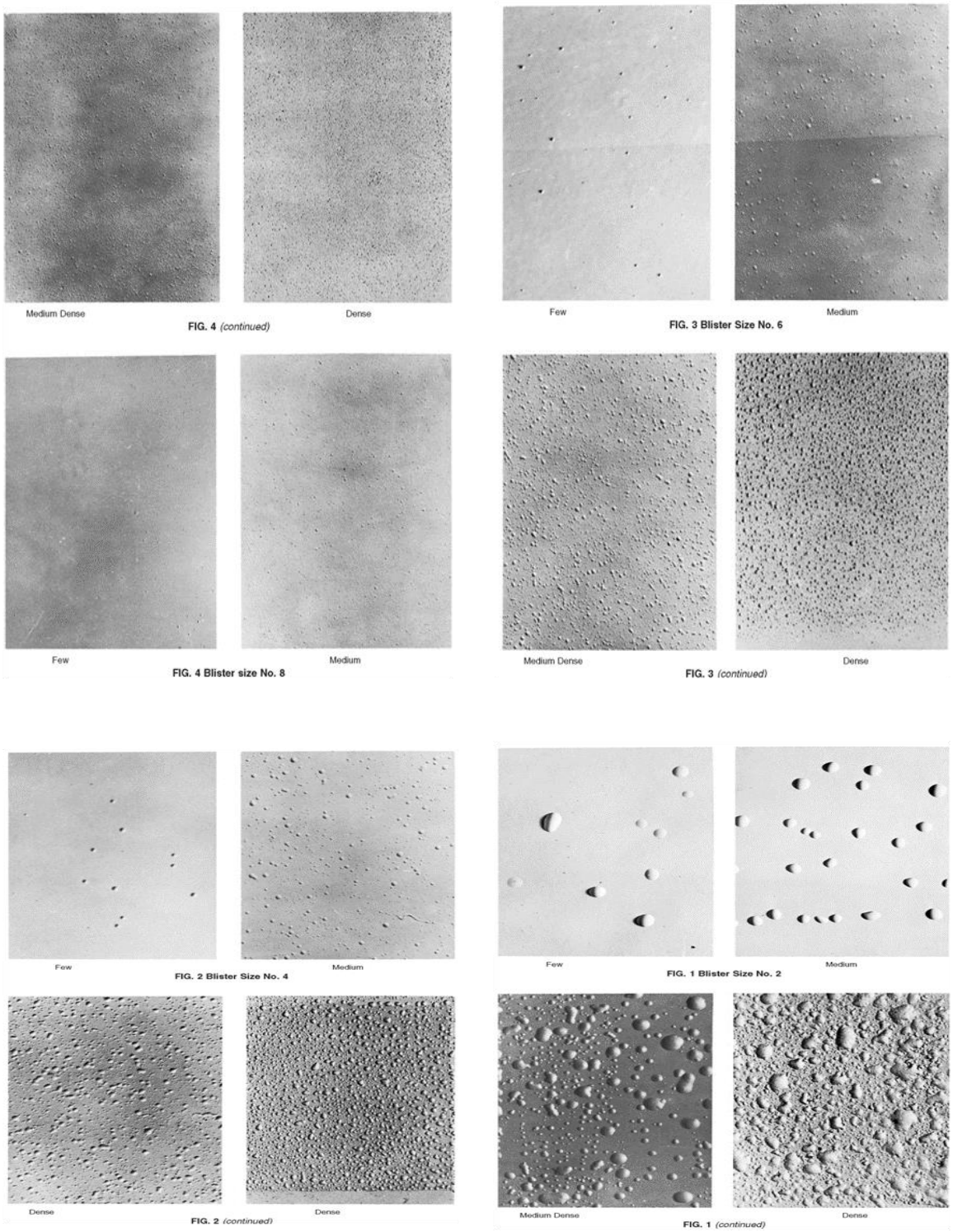



**Figure 10**: Rating Scale from ASTM D 714

#### 3.1.2.3 Moist Sulfur Dioxide ($SO_2$) Tests

Corrosion test panels were subjected to a 5% salt spray test with a periodic introduction of $SO_2$ gas directly into the chamber in accordance with ASTM G 85 Annex 4 [28]. The $SO_2$ gas was emitted into the test chamber for 1 hour every six hours (four times a day). The significant surface of the test panels was inclined 6º from the vertical. All test panels were exposed for 500 hours and rated in accordance with ASTM D 1654.

#### 3.1.2.4 Filiform Corrosion Resistance of Organic Coatings Testing

This test measures the ability of a coating system to protect the substrate against the formation of filiform corrosion [29]. An "X" incision is scribed through the coating so that the smaller angle of the "X" is 30° to 45°, making sure that the coating has been scribed all the way through and into the substrate. The scribe must have a 45° bevel, and each line of the "X" should be approximately 4 inches long. Place the scribed coupons in a desiccator containing 12 N hydrochloric acid (HCl) for one hour at 24 ± 3°C (75 ± 5°F). Within five minutes of removal from the desiccator, place the coupon in a humidity cabinet maintained at 40 ± 1.7°C (104 ± 3°F) and 80 ± 5 percent RH for 1,000 hours. Measure the length of any thread-like filaments at the end of the test duration and rating of pass/fail with MJ = majority of filiform and MN = minority of filiform present along scribe lines.

### 3.1.3 Additional Laboratory Testing

#### 3.1.3.1 Pencil Hardness (MIL-PRF-23377, MIL-PRF-85285)

Pencil hardness testing was performed in conjunction with crosshatch adhesion testing to provide baseline data and comparative data for use with JP-8 fluid immersion testing as described by MIL-PRF-23377 and MIL-PRF-85285 [30]. This test was performed on (*i*) primed and (*ii*) topcoated systems for AA 2024-T3 substrates only. UDRI/CTIO Laboratory Procedure CLG-LP-005, Pencil Hardness of Coatings, in accordance with ASTM D 3363, *Standard Test Method for Film Hardness by Pencil Test,* was used for guidance to run the test and to evaluate the samples. There were three replicates for each coating system, and the AA 2024-T3 panels used in the adhesion testing outlined in Section 3.0 were the same panels used in this test. The rating system from ASTM D 3363 is given in Figure 11.

$$\underbrace{6B-5B-4B-3B-2B-B-HB-F-H-2H-3H-4H-5H-6H}_{\text{Softer}\qquad\qquad\qquad\qquad\qquad\qquad\text{Harder}}$$

**Figure 11**: ASTM D 3363 Pencil Hardness Rating System

### 3.1.3.2 Impact Flexibility Testing (MIL-PRF-23377, MIL-PRF-85285)

One method of testing the flexibility of organic coatings is by using the GE Impact test instrument [31]. This test was performed on (*i*) primed and (*ii*) topcoated systems for AA 2024-T3 substrates only. UDRI/CTIO Laboratory Procedure CLG-LP-016, *GE Impact Flexibility Test*, in accordance with ASTM D 6905, *Standard Test Method for Impact Flexibility of Organic Coatings*, and MIL-PRF-85285 were used for guidance to run the test and to evaluate the flexibility of the samples. There were three replicates per coating system. Impact flexibility was tested by using a GE Model 172 reverse impact tester. Both ends of the indenter were dropped onto the test sample in reverse impact mode. The raised indentations produced on the sample were examined for signs of cracking and coating failure. The flexibility of the coating was determined by a visual examination of the coating at a magnification of 10X.

### 3.1.3.3 Hydraulic, Lubricating Oil, and JP-8 Fluid Resistance

Fluid resistance testing was performed to determine what effect can be expected by common aerospace fluids that come in contact with organic coatings. Hydraulic fluid and lubricating oil resistance tests were performed on

- (*i*) primed
- (*ii*) topcoated systems for AA 2024-T3 substrates only.

JP-8 fluid resistance testing was performed on topcoated systems for AA 2024-T3 substrates only. UDRI/CTIO Laboratory Procedures called out in CLG-LP-023, *Fluid Immersion—Hydraulic Fluid*, CLG-LP-024, *Fluid Immersion—Jet Fuel*, and CLG-LP-025, *Fluid Immersion—Lubricating Oil*, and conforming to MIL-PRF-23377 and MIL-PRF-85285, were used as the guidance documents to run the test and to evaluate the samples. The fluids were:

- MIL-PRF-83282, *Performance Specification, Hydraulic Fluid, Fire Resistant, Synthetic Hydrocarbon Base, Metric, NATO Code Number H-537*, at 66 ± 3°C,

- MIL-PRF-23699, *Performance Specification, Lubricating Oil, Aircraft Turbine Engine, Synthetic Base, NATO Code Number O-156*, at 121°C, and

- MIL-DTL-83133, *Detail Specification, Turbine Fuel, Aviation, Kerosene Type*, JP-8 jet fuel (without the +100 additive) at room temperature.

Initial crosshatch and pencil hardness values were taken from replicates exposed to the appropriate temperatures for the hydraulic fluid and lubricating oil tests and there were three replicates per coating system per test fluid.

#### 3.1.3.4 Physical Requirement: Surface Appearance (MIL-PRF-32239)

This requirement is part of MIL-PRF-32239. This test requires that the test panels, after a 24-hour ambient air-dry cure period at standard laboratory conditions, exhibit a uniform, smooth surface, free from runs, sags, bubbles, streaks, hazing, seeding, dusting, floating, mottling, or other defects. The presence of any defects were noted and reported and was given a "fail" rating. This test was performed on 2 samples from primed systems only for AA2024-T3 substrates. Surface appearance testing is a requirement under MIL-PRF-32239.

#### 3.1.3.5 Physical Requirement: Odor (MIL-PRF-32239)

This requirement is part of MIL-PRF-32239. This test was performed on Crosslink primer coated coupons, 48 hours after application for residual odor. In this test, coating materials were applied to test panels and left to dry for 48 hours at laboratory conditions. Each test panel was placed into a 1000 milliliter (mL) glass beaker that was covered and allowed to equilibrate for 20 minutes at room temperature. The beaker was uncovered and the presence of odor was checked. The presence of residual odor was cause for a "fail" rating. This test was performed on primed samples only for AA2024-T3 substrates.

#### 3.1.3.6 Physical Requirement: Drying Time (MIL-PRF-32239)

This requirement is part of MIL-PRF-32239. The Crosslink primer system was tested for drying time. Each component of the system (e.g., pretreatment, primer, or topcoat component of a full coating system) was tested using this method such that the end-user could apply the full system as rapidly and efficiently as possible. Per the requirement, coating system components designed to be surface pretreatments were expected to be dry and ready for primer within 4 hours of application. Coating system components that were designed to be primers were expected to be dry and ready for topcoat application within 5 hours. Coating system components designed to be topcoats were expected to be dry and ready for tape application with no loss of adhesion or permanent marring in 8 hours or less. An alternative measure of the total coating system application process was that the pretreatment, primer, and topcoat must reach the dry-to-tape condition in 17 hours or less. In MIL-PRF-32239, the drying time test method was different than the test method in some military specifications. After the coating (primer or topcoat) had reached the designated cure stage, 3M #250 masking tape or equivalent (1-inch wide) was applied to each test panel and left in place for 1 hour. When removed, it must not cause marring or loss of adhesion or a "fail" rating was noted. This test was performed on all primed systems for AA2024-T3 substrates after 5 hours of cure to document the performance of the system. Pretreatments were applied per normal laboratory practices. The test was performed only as a benchmark for performance of the Crosslink corrosion-inhibiting primer material in comparison to other materials.

#### 3.1.3.7 Reparability Testing

This test was a requirement for field test preparation. Reparability testing focused on the behavior of the material when applied as a repair coating to an existing system. The test method assumed that the standard system found on many USAF aircraft was the MIL-DTL-81706 (CCC), MIL-PRF-23377 chromated epoxy primer, and MIL-PRF-85285 ELT (topcoat). This is the system (chromated) for repair of or replacement with non-chromated coatings by changing the pretreatment or pretreatment and primer in the military coating system. Crosslink primer with various pretreatments (BAM-PPV and PreKote) was studied for their reparability.

**ALL FIGURES THROUGHOUT THIS DOCUMENT CONTAINING MULTIPLE SAMPLES ARE READ FROM LEFT TO RIGHT!**

# 4.0 Performance Assessment

## 4.1 Laboratory Testing

### 4.1.1 Laboratory Testing at WPAFB

#### 4.1.1.2 Adhesion Testing of Crosslink Primer Systems

##### 4.1.1.2.1 ASTM D 3359, Method B, Crosshatch Adhesion

This test performed by WPAFB followed ASTM D 3359 and is defined by ASTM as an implied adhesion test method which is "used to assess coating performance under actual service conditions." This test provided valuable information into "the approximate, relative level of adhesion" of the coating system. These ratings did not identify the layers of the coating system where loss of adhesion has occurred, rather only general information concerning the overall adhesion performance of the system was observed and recorded. The data obtained are only comparative in nature. This test was performed on (*i*) primed and (*ii*) topcoated systems for AA2024-T3 only. The ratings were assigned 4B to 5B and those coating meeting this matrix demonstrated a level of adhesion which was given a "pass" rating. This is consistent with the requirements in MIL-PRF-32239. The data are shown in Tables 11-12. The control system is highlighted in **green** and those systems with the Crosslink primer with acceptable performance are highlighted in **blue**.

**Table 11**: ASTM D 3359 Crosshatch Adhesion (Primed Systems)

| Coating System (No Topcoat) | Rating |
|---|---|
| **Pretreatment + Primer** | **AA 2024-T3 Data** |
| **Alodine 1600 + MIL-PRF-23377, chromated, Deft 02-Y-40** | **control 5B** |
| Alodine 1600 + MIL-PRF-23377, non-chromated, Deft 02-GN-084 | **pass 5B** |
| Alodine 1600 + MIL-PRF-23377, chromated, PPG, EEAY051 | **pass 5B** |
| Alodine 1600 + Crosslink primer | **pass 5B** |
| Alodine 5200 + MIL-PRF-23377, chromated, Deft 02-Y-40 | **pass 5B** |
| Alodine 5200 + MIL-PRF-23377, non-chromated, Deft 02-GN-084 | **pass 5B** |
| Alodine 5200 + MIL-PRF-23377, chromated, PPG, EEAY051 | **pass 5B** |
| Alodine 5200 + Crosslink primer | **pass 5B** |
| BAMPPV + MIL-PRF-23377, chromated, Deft 02-Y-40 | **pass 5B** |
| BAMPPV + MIL-PRF-23377, non-chromated, Deft 02-GN-084 | **pass 5B** |
| BAMPPV + MIL-PRF-23377, chromated, PPG, EEAY051 | **pass 5B** |
| BAMPPV + Crosslink primer | **pass 5B** |
| Prekote + MIL-PRF-23377, chromated, Deft 02-Y-40 | **pass 5B** |
| Prekote + MIL-PRF-23377, non-chromated, Deft 02-GN-084 | **pass 5B** |
| Prekote + MIL-PRF-23377, chromated, PPG, EEAY051 | **pass 5B** |
| Prekote + Crosslink primer | **pass 5B** |

**Table 12**: ASTM D 3359 Crosshatch Adhesion (MIL-PRF-85285 Topcoated Systems)

| Coating System | Rating |
|---|---|
| **Pretreatment +<br>Primer +<br>Topcoat** | **AA 2024-T3<br>Data** |
| **Alodine 1600 +<br>MIL-PRF-23377, chromated, Deft 02-Y-40<br>MIL-PRF-85285, Deft ELT, 99-GY-001** | **control<br>4B** |
| Alodine 1600 +<br>MIL-PRF-23377, non-chromated, Deft 02-GN-084<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | **pass<br>5B** |
| Alodine 1600 +<br>Crosslink primer +<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | **pass<br>5B** |
| Alodine 1600 +<br>MIL-PRF-23377, chromated, PPG, EEAY051<br>MIL-PRF-85285, PPG ELT, CA9311 | **pass<br>4B** |
| Alodine 1600 +<br>Crosslink primer<br>MIL-PRF-85285, PPG ELT, CA9311 | **pass<br>4B** |
| Alodine 5200 +<br>MIL-PRF-23377, chromated, Deft 02-Y-40<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | **pass<br>4B** |
| Alodine 5200 +<br>MIL-PRF-23377, non-chromated, Deft 02-GN-084<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | **pass<br>4B** |
| Alodine 5200 +<br>Crosslink primer<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | **pass<br>5B** |
| Alodine 5200 +<br>MIL-PRF-23377, chromated, PPG, EEAY051<br>MIL-PRF-85285, PPG ELT, CA9311 | **pass<br>5B** |
| Alodine 5200 +<br>Crosslink primer<br>MIL-PRF-85285, PPG ELT, CA9311 | **pass<br>5B** |
| BAMPPV +<br>MIL-PRF-23377, chromated, Deft 02-Y-40<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | **pass<br>5B** |
| BAMPPV +<br>MIL-PRF-23377, non-chromated, Deft 02-GN-084<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | **pass<br>5B** |
| BAMPPV +<br>Crosslink primer<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | **pass<br>5B** |
| BAMPPV +<br>MIL-PRF-23377, chromated, PPG, EEAY051<br>MIL-PRF-85285, PPG ELT, CA9311 | **pass<br>4B** |
| BAMPPV +<br>Crosslink primer<br>MIL-PRF-85285, PPG ELT, CA9311 | **pass<br>5B** |

| | |
|---|---|
| Prekote +<br>MIL-PRF-23377, chromated, Deft 02-Y-40<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | **pass**<br>**5B** |
| Prekote +<br>MIL-PRF-23377, non-chromated, Deft 02-GN-084<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | **pass**<br>**5B** |
| Prekote +<br>Crosslink primer<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | **pass**<br>**5B** |
| Prekote +<br>MIL-PRF-23377, chromated, PPG, EEAY051<br>MIL-PRF-85285, PPG ELT, CA9311 | **pass**<br>**5B** |
| Prekote +<br>Crosslink primer<br>MIL-PRF-85285, PPG ELT, CA9311 | **pass**<br>**5B** |

#### 4.1.1.2.2 FTMS 141D, Method 6301, Wet-tape Adhesion

This test is outlined in the Federal Test Method Standard 141 as an inter-coat and surface adhesion test for organic systems immersed in water. The rating system from ASTM D 3359, Method A, was used to determine a pass/fail condition for the coating system. These ratings do not distinguish between inter-coat, intra-coat, and substrate interface failure modes. The rating determined by this test which have a 4A or higher were rated as "pass" and are highlighted in **blue**. Any ratings that are below 3A are poor performers and highlighted in **red** and the control system is highlighted in **green** (See Tables 13-14).

**Table 13**: FTMS 141, ASTM D 3359 Wet Tape Adhesion (Primed Systems)

| Coating System (No Topcoat) | Rating |
|---|---|
| **Pretreatment + Primer** | **AA 2024-T3 Data** |
| **Alodine 1600 + MIL-PRF-23377, chromated, Deft 02-Y-40** | **control 5A** |
| Alodine 1600 + MIL-PRF-23377, non-chromated, Deft 02-GN-084 | **pass 5A** |
| Alodine 1600 + MIL-PRF-23377, chromated, PPG, EEAY051 | **pass 5A** |
| Alodine 1600 + Crosslink primer | **pass 5A** |
| Alodine 5200 + MIL-PRF-23377, chromated, Deft 02-Y-40 | **pass 5A** |
| Alodine 5200 + MIL-PRF-23377, non-chromated, Deft 02-GN-084 | **pass 5A** |
| Alodine 5200 + MIL-PRF-23377, chromated, PPG, EEAY051 | **pass 5A** |
| Alodine 5200 + Crosslink primer | **pass 5A** |
| BAMPPV + MIL-PRF-23377, chromated, Deft 02-Y-40 | **pass 4A** |
| BAMPPV + MIL-PRF-23377, non-chromated, Deft 02-GN-084 | **pass 4A** |
| BAMPPV + MIL-PRF-23377, chromated, PPG, EEAY051 | **fail 0A** |
| BAMPPV + Crosslink primer | **fail 0A** |
| Prekote + MIL-PRF-23377, chromated, Deft 02-Y-40 | **pass 5A** |
| Prekote + MIL-PRF-23377, non-chromated, Deft 02-GN-084 | **pass 5A** |
| Prekote + MIL-PRF-23377, chromated, PPG, EEAY051 | **pass 5A** |
| Prekote + Crosslink primer | **fail 0A** |

**Table 14**: FTMS 141, ASTM D 3359 Wet Tape Adhesion (MIL-PRF-85285 Topcoated Systems)

| Coating System | Rating |
|---|---|
| **Pretreatment + Primer + Topcoat** | **AA 2024-T3 Data** |
| **Alodine 1600 + MIL-PRF-23377, chromated, Deft 02-Y-40 MIL-PRF-85285, Deft ELT, 99-GY-001** | **control 4A** |
| Alodine 1600 + MIL-PRF-23377, non-chromated, Deft 02-GN-084 MIL-PRF-85285, Deft ELT, 99-GY-001 | **pass 5A** |
| Alodine 1600 + Crosslink primer + MIL-PRF-85285, Deft ELT, 99-GY-001 | **pass 5A** |
| Alodine 1600 + MIL-PRF-23377, chromated, PPG, EEAY051 MIL-PRF-85285, PPG ELT, CA9311 | **pass 5A** |
| Alodine 1600 + Crosslink primer MIL-PRF-85285, PPG ELT, CA9311 | **pass 5A** |
| Alodine 5200 + MIL-PRF-23377, chromated, Deft 02-Y-40 MIL-PRF-85285, Deft ELT, 99-GY-001 | **pass 5A** |
| Alodine 5200 + MIL-PRF-23377, non-chromated, Deft 02-GN-084 MIL-PRF-85285, Deft ELT, 99-GY-001 | **pass 5A** |
| Alodine 5200 + Crosslink primer MIL-PRF-85285, Deft ELT, 99-GY-001 | **pass 5A** |
| Alodine 5200 + MIL-PRF-23377, chromated, PPG, EEAY051 MIL-PRF-85285, PPG ELT, CA9311 | **pass 5A** |
| Alodine 5200 + Crosslink primer MIL-PRF-85285, PPG ELT, CA9311 | **pass 5A** |

The data suggested that the BAM-PPV material was not compatible with the Crosslink corrosion-inhibiting primer formulation. It also suggested that the Crosslink corrosion-inhibiting primer was not compatible with PreKote. Because there was the potential that the results were from the high molecular weight issue with the BAM-PPV, retesting was suggested for the Crosslink corrosion-inhibiting primer and BAM-PPV systems using a new batch of BAM-PPV that had been corrected for the high molecular weight issue. The systems in Table 15 were retested for wet tape adhesion. The results are found in Table 16. Photographs of coating performance are given in Figures 12-13. The replicate data confirm that the new BAM-PPV material performed as expected from previous testing with no compatibility issues noted with the MIL-PRF-23377 materials. The Crosslink corrosion-inhibiting primer did not demonstrate a change in performance and, instead, demonstrated a compatibility issue with the BAM-PPV material. The data

suggested that the application of the Crosslink corrosion-inhibiting primer compromised the BAM-PPV material by dissolving the material and causing it to be porous and have a weak bond to the substrate. Overall, these results suggest a compatibility issue between the Crosslink corrosion-inhibiting primer and other materials in use in military coating systems.

**Table 15**: Systems Retested using BAM-PPV and Crosslink Corrosion-Inhibiting Primer

| Pretreatment | Primer | Topcoat |
|---|---|---|
| BAM-PPV | MIL-PRF-23377, chromated, Deft 02-Y-40 | None |
| | | MIL-PRF-85285, Deft ELT, 99-GY-001 |
| | MIL-PRF-23377, chromated, Deft 02-Y-40 | None |
| | | MIL-PRF-85285, Deft ELT, 99-GY-001 |
| | Crosslink Primer | None |
| | | MIL-PRF-85285, Deft ELT, 99-GY-001 |

**Table 16**: Results from Retest, Wet Tape Adhesion

| **Coating System** | **Rating** |
|---|---|
| **Pretreatment + Primer + Topcoat** | **AA 2024-T3 Data** |
| BAMPPV + MIL-PRF-23377, chromated, Deft 02-Y-40 (No Topcoat) | **pass 4A** |
| BAMPPV + MIL-PRF-23377, non-chromated, Deft 02-GN-084 (No Topcoat) | **pass 5A** |
| BAMPPV + Crosslink primer (No Topcoat) | **fail 0A** |
| BAMPPV + MIL-PRF-23377, chromated, Deft 02-Y-40 MIL-PRF-85285, Deft ELT, 99-GY-001 | **pass 4A** |
| BAMPPV + MIL-PRF-23377, non-chromated, Deft 02-GN-084 MIL-PRF-85285, Deft ELT, 99-GY-001 | **pass 5A** |
| BAMPPV + Crosslink primer MIL-PRF-85285, Deft ELT, 99-GY-001 | **fail 0A** |

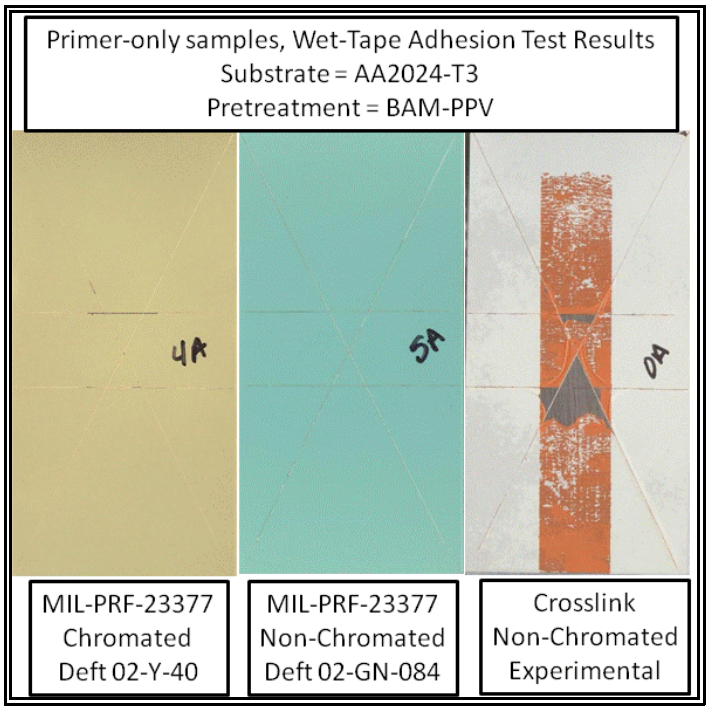



**Figure 12**: Primer-Only Samples on AA2024-T3, Wet Tape Adhesion Test Results: Pretreatment, Non-Chromated Coating, BAM-PPV (Repeated Testing)

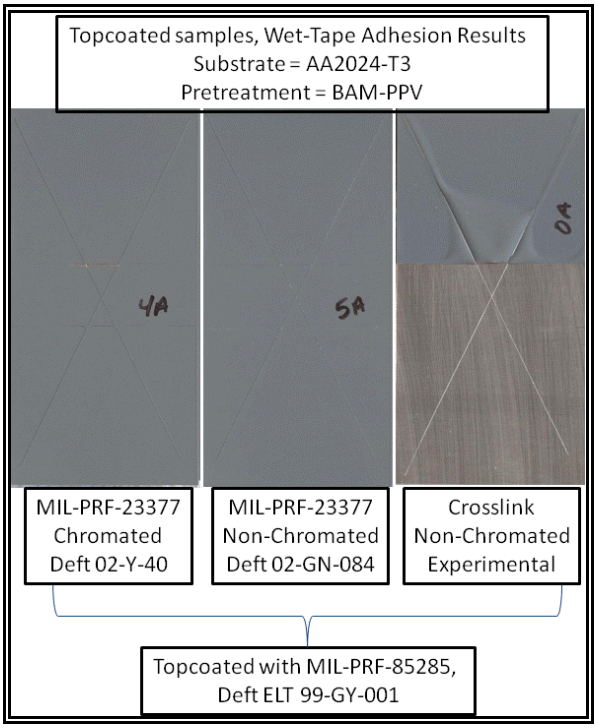



**Figure 13**: Topcoated Salt Spray Samples on AA2024-T3, Wet Tape Adhesion Test Results: Pretreatment, Non-Chromated Coating, BAM-PPV (Repeated Testing)

#### 4.1.1.2.3 ASTM D4541 Patti, Pull-off Adhesion

PATTI pull-off adhesion was conducted on the Crosslink primer system with various pretreatment and topcoat combinations. The following criteria were applied to the data to determine outliers, suspect data, and confidence intervals. ASTM recommends that a statistical analysis for outliers is performed on all data sets to reject unreliable numerical pull-off values and the data that were obtained are numerical and quantitative, but all failure modes qualitative. Therefore, ASTM recommends that the numerical value for the pull-off be disregarded when more than 50% of the failure mode was the result of adhesive failure. The data obtained for the Crosslink primer systems are found in Tables 17-18. The assignment of pass/fail for a coating system was based largely upon consideration of the average pull-off value and failure mode in comparison to that of the control. All the data presented in Tables 17-18 are comparative in nature. This test was performed on (*i*) primed and (*ii*) topcoated systems and most of the systems tested demonstrated acceptable adhesion behavior in this test. No system ratings for pass/fail are assigned. The control system is highlighted in **green**. The best performing system using the Crosslink primer included the Cr(VI) pretreatment and Prekote. The worst performing system using the Crosslink primer was with the BAM-PPV pretreatment.

**Table 17**: ASTM D 4541 Pull-Off Adhesion (Primed Systems)

| **Coating System (No Topcoat)** | **Rating** | |
|---|---|---|
| **Pretreatment + Primer** | **Pull-Off Value (psi)** | **Failure Mode** |
| **Alodine 1600 + MIL-PRF-23377, chromated, Deft 02-Y-40** | **control 1422** | **P / P** |
| Alodine 1600 + MIL-PRF-23377, non-chromated, Deft 02-GN-084 | 1813 | P / S and P / P |
| Alodine 1600 + MIL-PRF-23377, chromated, PPG, EEAY051 | 1895 | P / S and P / P |
| Alodine 1600 + Crosslink primer | 1238 | P / S and P / P |
| Alodine 5200 + MIL-PRF-23377, chromated, Deft 02-Y-40 | 1310 | P / P |
| Alodine 5200 + MIL-PRF-23377, non-chromated, Deft 02-GN-084 | 974 | P / P and P / E |
| Alodine 5200 + MIL-PRF-23377, chromated, PPG, EEAY051 | 1563 | P / S and P / P |
| Alodine 5200 + Crosslink primer | 1240 | P / S and P / P |
| BAMPPV + MIL-PRF-23377, chromated, Deft 02-Y-40 | 1353 | P / P |
| BAMPPV + MIL-PRF-23377, non-chromated, Deft 02-GN-084 | 967 | Pretreat / Pretreat |
| BAMPPV + MIL-PRF-23377, chromated, PPG, EEAY051 | 951 | Pretreat / Pretreat |
| BAMPPV + Crosslink primer | 988 | Pretreat / Pretreat |

| | | |
|---|---|---|
| Prekote +<br>MIL-PRF-23377, chromated, Deft 02-Y-40 | 1216 | P / P |
| Prekote +<br>MIL-PRF-23377, non-chromated, Deft 02-GN-084 | 1493 | P / P and<br>P / E |
| Prekote +<br>MIL-PRF-23377, chromated, PPG, EEAY051 | 1083 | P / P and<br>P / E |
| Prekote +<br>Crosslink primer | 1256 | P / P |

**Table 18**: ASTM D 4541 Pull-Off Adhesion (MIL-PRF-85285 Topcoated Systems)

| **Coating System** | **Rating** | |
|---|---|---|
| **Pretreatment +<br>Primer +<br>Topcoat** | **Pull-Off Value<br>(psi)** | **Failure Mode** |
| **Alodine 1600 +<br>MIL-PRF-23377, chromated, Deft 02-Y-40<br>MIL-PRF-85285, Deft ELT, 99-GY-001** | **control<br>1541** | **P / P** |
| Alodine 1600 +<br>MIL-PRF-23377, non-chromated, Deft 02-GN-084<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | 1311 | P / P |
| Alodine 1600 +<br>Crosslink primer +<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | 1936 | P / S |
| Alodine 1600 +<br>MIL-PRF-23377, chromated, PPG, EEAY051<br>MIL-PRF-85285, PPG ELT, CA9311 | 1947 | P / P |
| Alodine 1600 +<br>Crosslink primer<br>MIL-PRF-85285, PPG ELT, CA9311 | 1982 | P / S |
| Alodine 5200 +<br>MIL-PRF-23377, chromated, Deft 02-Y-40<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | 1806 | P / P |
| Alodine 5200 +<br>MIL-PRF-23377, non-chromated, Deft 02-GN-084<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | 1735 | P / P and<br>P / S |
| Alodine 5200 +<br>Crosslink primer<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | 1898 | P / S |
| Alodine 5200 +<br>MIL-PRF-23377, chromated, PPG, EEAY051<br>MIL-PRF-85285, PPG ELT, CA9311 | 1927 | P / P |
| Alodine 5200 +<br>Crosslink primer<br>MIL-PRF-85285, PPG ELT, CA9311 | 1957 | P / S |
| BAMPPV +<br>MIL-PRF-23377, chromated, Deft 02-Y-40<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | 1984 | P / S |
| BAMPPV +<br>MIL-PRF-23377, non-chromated, Deft 02-GN-084 | 1973 | P / S and<br>P / Pretreat |

| | | |
|---|---|---|
| MIL-PRF-85285, Deft ELT, 99-GY-001 | | |
| BAMPPV +<br>Crosslink primer<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | 1701 | P / Pretreat |
| BAMPPV +<br>MIL-PRF-23377, chromated, PPG, EEAY051<br>MIL-PRF-85285, PPG ELT, CA9311 | 1566 | P / S and<br>P / Pretreat |
| BAMPPV +<br>Crosslink primer<br>MIL-PRF-85285, PPG ELT, CA9311 | 1873 | P / Pretreat |
| Prekote +<br>MIL-PRF-23377, chromated, Deft 02-Y-40<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | 1794 | P / P |
| Prekote +<br>MIL-PRF-23377, non-chromated, Deft 02-GN-084<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | 1548 | P / P |
| Prekote +<br>Crosslink primer<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | 1431 | P / S |
| Prekote +<br>MIL-PRF-23377, chromated, PPG, EEAY051<br>MIL-PRF-85285, PPG ELT, CA9311 | 1419 | P / P |
| Prekote +<br>Crosslink primer<br>MIL-PRF-85285, PPG ELT, CA9311 | 1377 | P / S |

#### 4.1.1.3 Accelerated Weathering Testing of Crosslink Primer Systems

##### 4.1.1.3.1 Neutral Salt Spray (NSS) Testing

The Crosslink primer in various combinations with pretreatment and topcoats were exposed to NSS testing. The initial studies showed that these non-chromated coating systems displayed poor performance at 2000 hours. The testing was suspended after 2000 hours of NSS exposure. The rating systems for primed and topcoated samples exposed to salt spray for 2000 hours are found in Tables 19-21 and are derived from ASTM methods and historical practices for military specification interpretations and please refer to Section 3.1.2.1. The data for primed systems are in Table 22, and photographs for those systems are in Figures 14-21. The data for topcoated systems are in Tables 23-24, and photographs for those systems are in Figures 22-28. Ratings are listed along with an interpretation rating of “acceptable,” “low,” or “poor.”

An interpretation rating of “acceptable” is

- minor corrosion in the scribe (a rating no greater than 2) with no undercutting or blisters (that is, ratings of 0 for these categories).

An interpretation rating of “low” is

- minor corrosion in the scribe (no greater than 2) in combination with undercutting no greater than 1 or blistering equal to 1.

A “low” rating was also given to systems

- with a "corrosion in the scribe" rating of "3" and no undercutting or blistering (i.e., rating 3 0 0).

An interpretation rating of "poor" is

- any combination of ratings for corrosion, undercutting, or blistering that is greater than the previous two mentioned.

For example, a rating of 2 0 0 is considered "acceptable" performance and is comparable to control data. A rating of 2 0 1 is considered "low" performance. A rating of 2 3 0 or 2 2 1 is considered "poor" performance because it does not provide comparable performance. In some cases, the control system is also rated with "low" performance. This may be the result of batch differences of the materials; however, to maintain comparability to other testing previously performed, the rating is described similarly to previous ratings. Acceptable ratings are highlighted in **blue**. Poor ratings are highlighted in **red**. Control systems are highlighted in **green**.

**Table 19**: Salt Spray Ratings (2000 hours) (Primed Systems)

| **Coating System (No Topcoat)** | **Rating** | |
|---|---|---|
| **Pretreatment + Primer** | **AA2024-T3 Data** | **AA7075-T6 Data** |
| **Alodine 1600 + MIL-PRF-23377, chromated, Deft 02-Y-40** | **control 2 0 0** | **control 1 0 0** |
| Alodine 1600 + MIL-PRF-23377, non-chromated, Deft 02-GN-084 | low 3 0 0 | **acceptable 2 0 0** |
| Alodine 1600 + MIL-PRF-23377, chromated, PPG, EEAY051 | **acceptable 0 0 0** | **acceptable 1 0 0** |
| Alodine 1600 + Crosslink primer | **acceptable 1 0 0** | **acceptable 1 0 0** |
| Alodine 5200 + MIL-PRF-23377, chromated, Deft 02-Y-40 | **acceptable 1 0 0** | **acceptable 1 0 0** |
| Alodine 5200 + MIL-PRF-23377, non-chromated, Deft 02-GN-084 | **poor 3 1 2** | **poor 2 1 2** |
| Alodine 5200 + MIL-PRF-23377, chromated, PPG, EEAY051 | **acceptable 0 0 0** | **poor 1 0 1** |
| Alodine 5200 + Crosslink primer | **poor 3 0 1** | **poor 3 1 1** |
| BAMPPV + MIL-PRF-23377, chromated, Deft 02-Y-40 | **acceptable 1 0 0** | **poor 1 0 2** |
| BAMPPV + MIL-PRF-23377, non-chromated, Deft 02-GN-084 | **poor 3 0 3** | **poor 2 1 3** |
| BAMPPV + MIL-PRF-23377, chromated, PPG, EEAY051 | **poor 0 2 3** | **poor 1 0 2** |
| BAMPPV + Crosslink primer | **poor 2 0 3** | **poor 2 0 2** |
| Prekote + MIL-PRF-23377, chromated, Deft 02-Y-40 | **acceptable 1 0 0** | **acceptable 1 0 0** |
| Prekote + MIL-PRF-23377, non-chromated, Deft 02-GN-084 | **poor 2 1 2** | **poor 2 3 2** |

| | | |
|---|---|---|
| Prekote +<br>MIL-PRF-23377, chromated, PPG, EEAY051 | **acceptable**<br>**0 0 0** | **acceptable**<br>**0 0 0** |
| Prekote +<br>Crosslink primer | **poor**<br>**1 0 1** | **poor**<br>**1 1 1** |

**Table 20**: Salt Spray Ratings (2000 hours) using Alodine 1600 and 5200 (MIL-PRF-85285 Topcoated Systems)

| **Coating System** | **Rating** | |
|---|---|---|
| **Pretreatment +<br>Primer +<br>Topcoat** | **AA 2024-T3 Data** | **AA 7075-T6 Data** |
| **Alodine 1600 +<br>MIL-PRF-23377, chromated, Deft 02-Y-40<br>MIL-PRF-85285, Deft ELT, 99-GY-001** | **control**<br>**3 1 0** | **control**<br>**2 1 0** |
| Alodine 1600 +<br>MIL-PRF-23377, non-chromated, Deft 02-GN-084<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | low<br>3 0 0 | **acceptable**<br>**2 0 0** |
| Alodine 1600 +<br>Crosslink primer +<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | low<br>3 0 0 | low<br>2 1 0 |
| Alodine 1600 +<br>MIL-PRF-23377, chromated, PPG, EEAY051<br>MIL-PRF-85285, PPG ELT, CA9311 | low<br>2 1 0 | **acceptable**<br>**1 0 0** |
| Alodine 1600 +<br>Crosslink primer<br>MIL-PRF-85285, PPG ELT, CA9311 | low<br>2 1 0 | low<br>2 1 0 |
| Alodine 5200 +<br>MIL-PRF-23377, chromated, Deft 02-Y-40<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | **poor**<br>**3 1 0** | **acceptable**<br>**2 0 0** |
| Alodine 5200 +<br>MIL-PRF-23377, non-chromated, Deft 02-GN-084<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | **poor**<br>**3 1 0** | low<br>2 1 0 |
| Alodine 5200 +<br>Crosslink primer<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | low<br>2 1 0 | **poor**<br>**2 2 0** |
| Alodine 5200 +<br>MIL-PRF-23377, chromated, PPG, EEAY051<br>MIL-PRF-85285, PPG ELT, CA9311 | low<br>2 1 0 | **acceptable**<br>**1 0 0** |
| Alodine 5200 +<br>Crosslink primer<br>MIL-PRF-85285, PPG ELT, CA9311 | low<br>2 1 0 | **poor**<br>**2 3 0** |

**Table 21**: Salt Spray Ratings (2000 hours) using BAM-PPV and Prekote Pretreatments (MIL-PRF-85285 Topcoated Systems)

| **Coating System** | **Rating** | |
|---|---|---|
| **Pretreatment + Primer + Topcoat** | **AA 2024-T3 Data** | **AA 7075-T6 Data** |
| BAMPPV +<br>MIL-PRF-23377, chromated, Deft 02-Y-40<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | **poor**<br>**3 5 0** | **poor**<br>**2 3 0** |
| BAMPPV +<br>MIL-PRF-23377, non-chromated, Deft 02-GN-084<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | **poor**<br>**3 4 0** | **poor**<br>**2 5 0** |
| BAMPPV +<br>Crosslink primer<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | **poor**<br>**3 5 5** | **poor**<br>**2 5 2**<br>**gator skin** |
| BAMPPV +<br>MIL-PRF-23377, chromated, PPG, EEAY051<br>MIL-PRF-85285, PPG ELT, CA9311 | **poor**<br>**3 4 0** | **poor**<br>**1 0 2** |
| BAMPPV +<br>Crosslink primer<br>MIL-PRF-85285, PPG ELT, CA9311 | **poor**<br>**3 5 5** | **poor**<br>**2 5 0** |
| Prekote +<br>MIL-PRF-23377, chromated, Deft 02-Y-40<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | low<br>3 0 0 | **poor**<br>**2 3 0** |
| Prekote +<br>MIL-PRF-23377, non-chromated, Deft 02-GN-084<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | **poor**<br>**3 1 0** | **poor**<br>**2 3 2** |
| Prekote +<br>Crosslink primer<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | **poor**<br>**2 5 5** | **poor**<br>**2 5 0** |
| Prekote +<br>MIL-PRF-23377, chromated, PPG, EEAY051<br>MIL-PRF-85285, PPG ELT, CA9311 | low<br>3 0 0 | **acceptable**<br>**1 0 0** |
| Prekote +<br>Crosslink primer<br>MIL-PRF-85285, PPG ELT, CA9311 | **poor**<br>**2 5 5** | **poor**<br>**2 5 0** |

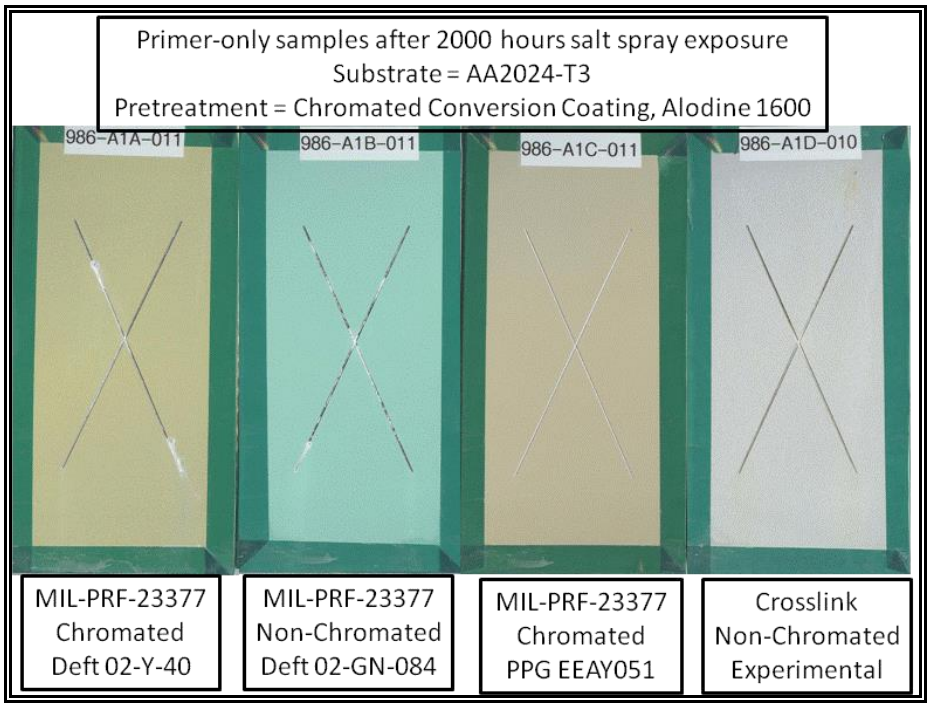



**Figure 14**: Primer-Only Salt Spray Samples on AA2024-T3 after 2000 hours of Exposure: Pretreatment, Chromated Conversion Coating, Alodine 1600

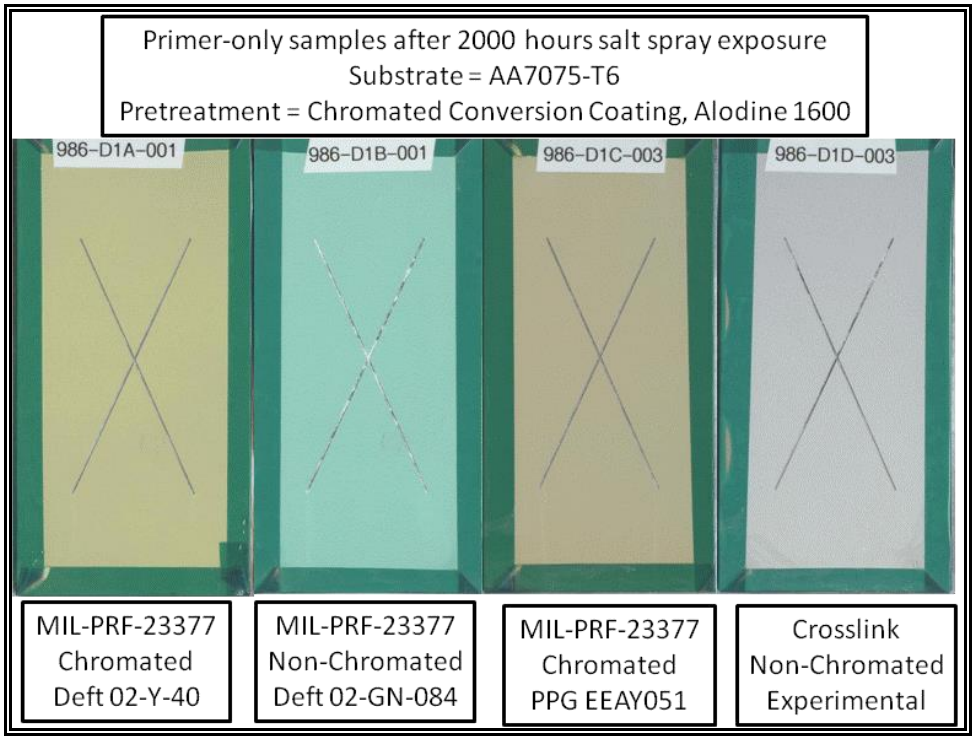



**Figure 15**: Primer-Only Salt Spray Samples on AA7075-T6 after 2000 hours of Exposure: Pretreatment, Chromated Conversion Coating, Alodine 1600

**Figure 16**: Primer-Only Salt Spray Samples on AA2024-T3 after 2000 hours of Exposure: Pretreatment, Non-Chromated Conversion Coating, Alodine 5200

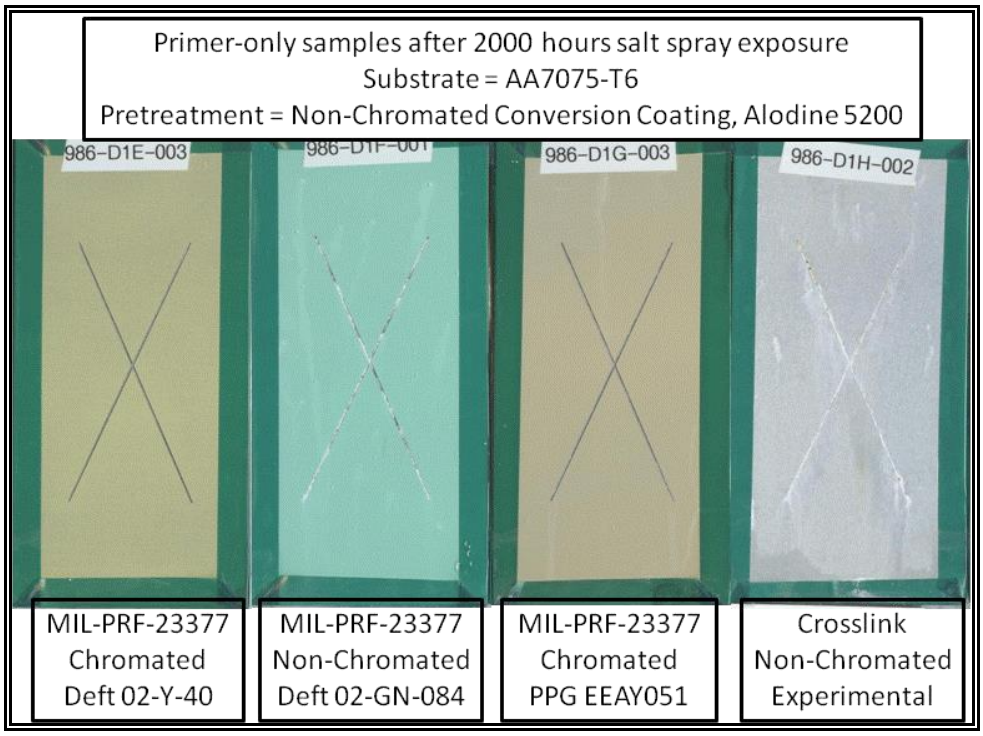



**Figure 17**: Primer-Only Salt Spray Samples on AA7075-T6 after 2000 hours of Exposure: Pretreatment, Non-Chromated Conversion Coating, Alodine 5200

**Figure 18**: Primer-Only Salt Spray Samples on AA2024-T3 after 2000 hours of Exposure: Pretreatment, Non-Chromated Coating, BAM-PPV

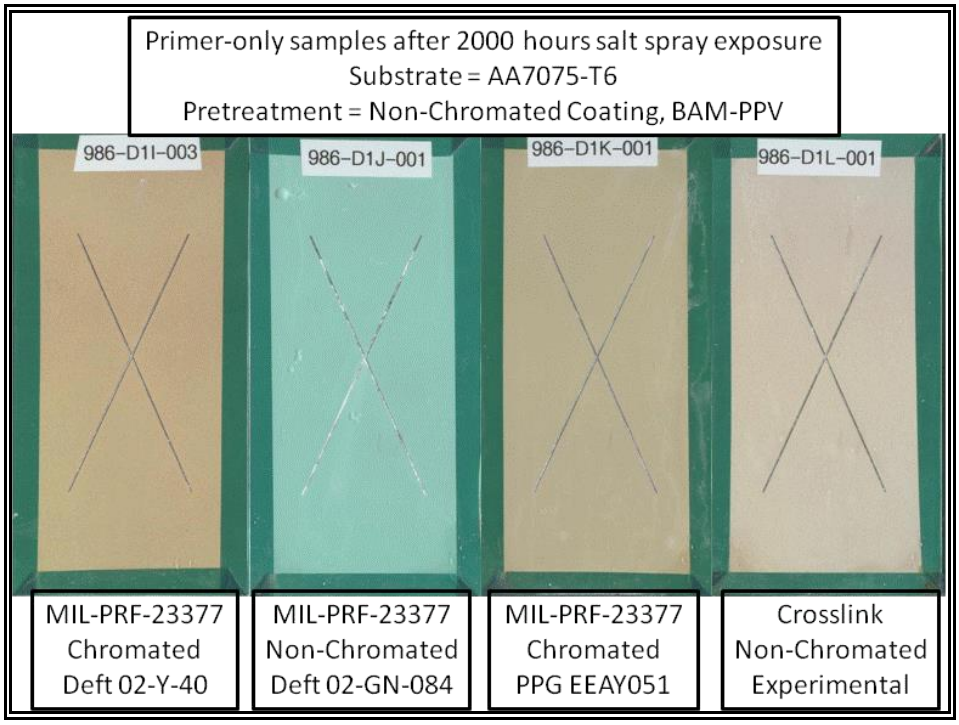



**Figure 19**: Primer-Only Salt Spray Samples on AA7075-T6 after 2000 hours of Exposure: Pretreatment, Non-Chromated Coating, BAM-PPV

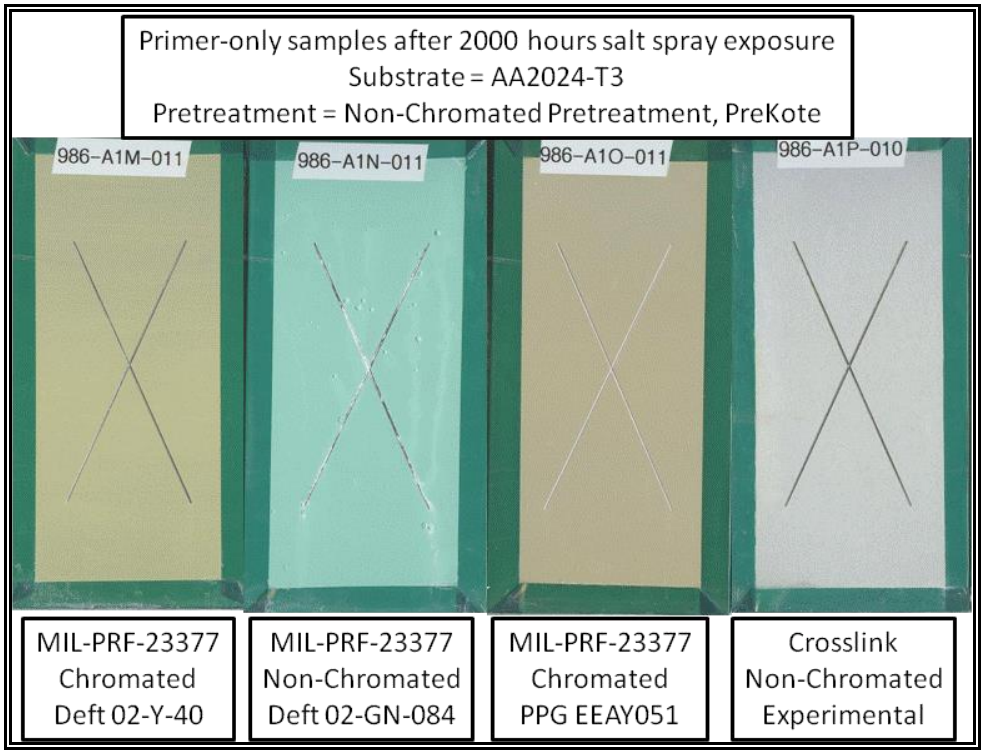



**Figure 20**: Primer-Only Salt Spray Samples on AA2024-T3 after 2000 hours of Exposure: Pretreatment, Non-Chromated Surface Pretreament, PreKote

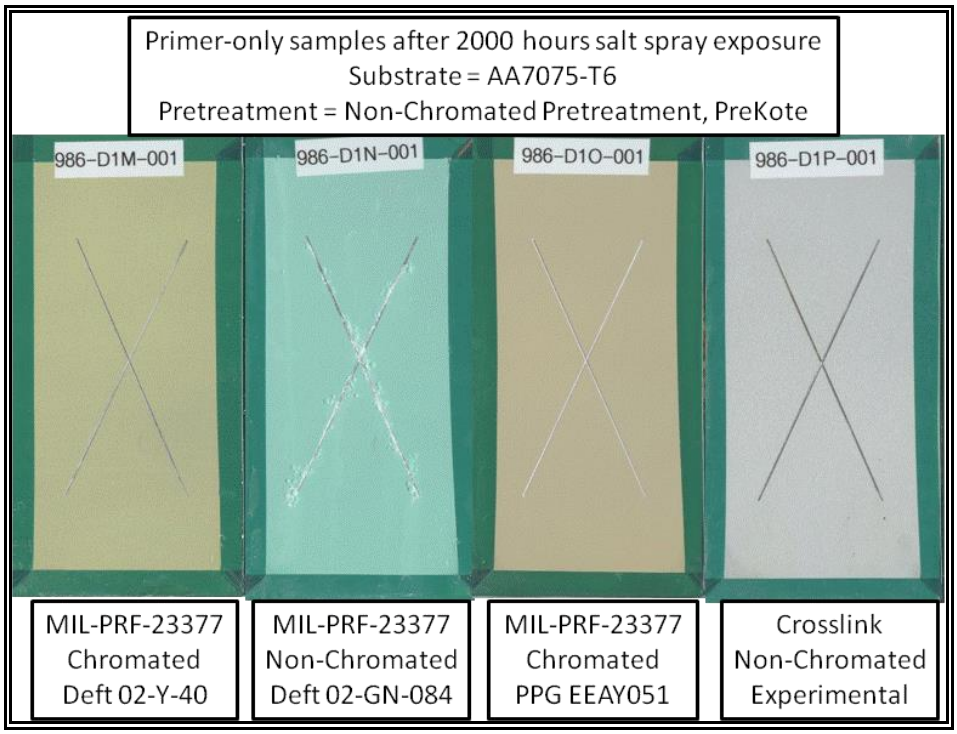



**Figure 21**: Primer-Only Salt Spray Samples on AA7075-T6 after 2000 hours of Exposure: Pretreatment, Non-Chromated Surface Pretreatment, PreKote

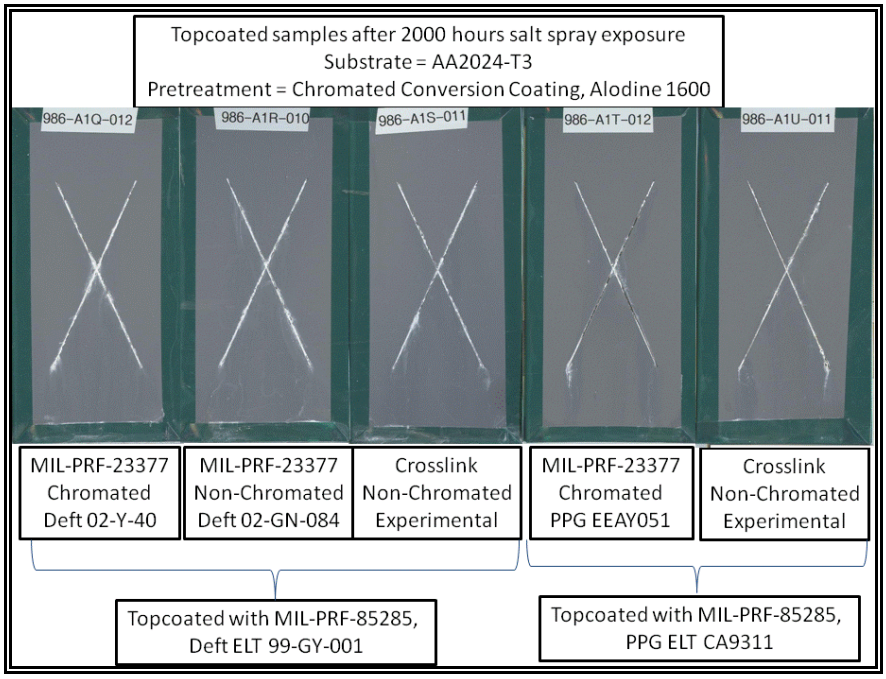



**Figure 22**: Topcoated Salt Spray Samples on AA2024-T3 after 2000 hours of Exposure: Pretreatment, Chromated Conversion Coating, Alodine 1600

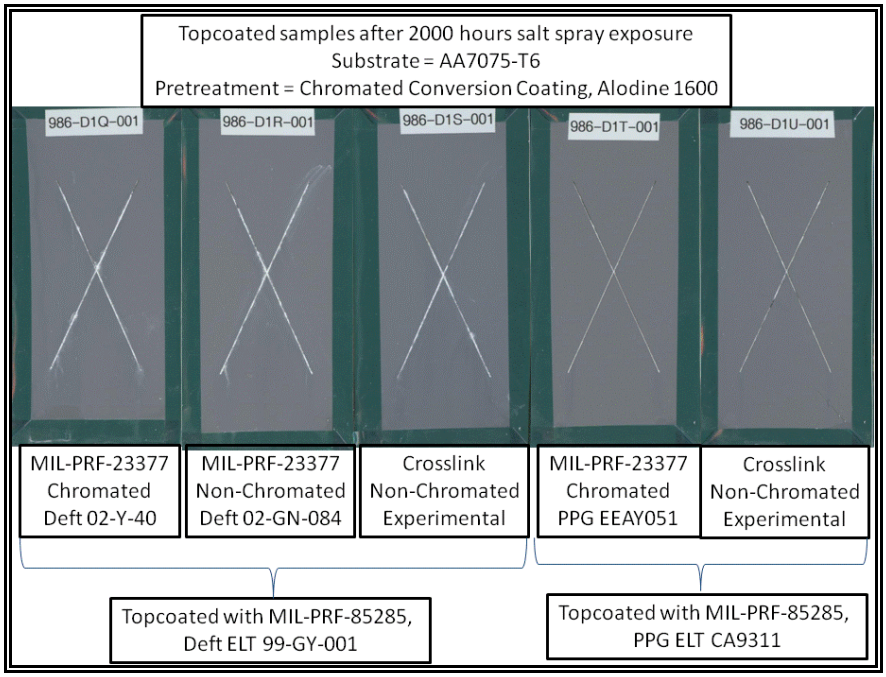



**Figure 23**: Topcoated Salt Spray Samples on AA7075-T6 after 2000 hours of Exposure: Pretreatment, Chromated Conversion Coating, Alodine 1600

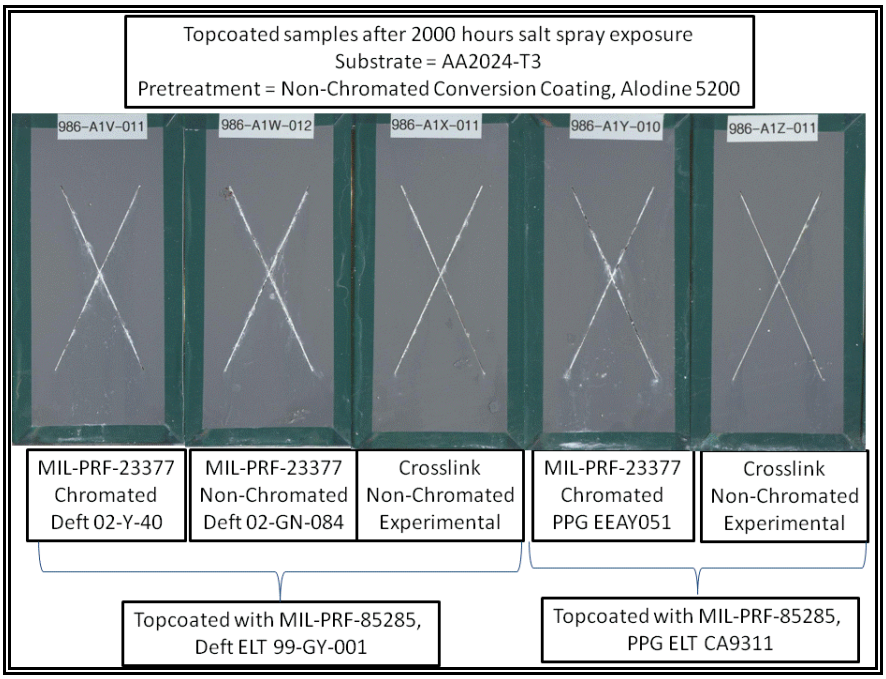



**Figure 24**: Topcoated Salt Spray Samples on AA2024-T3 after 2000 hours of Exposure: Pretreatment, Non-Chromated Conversion Coating, Alodine 5200

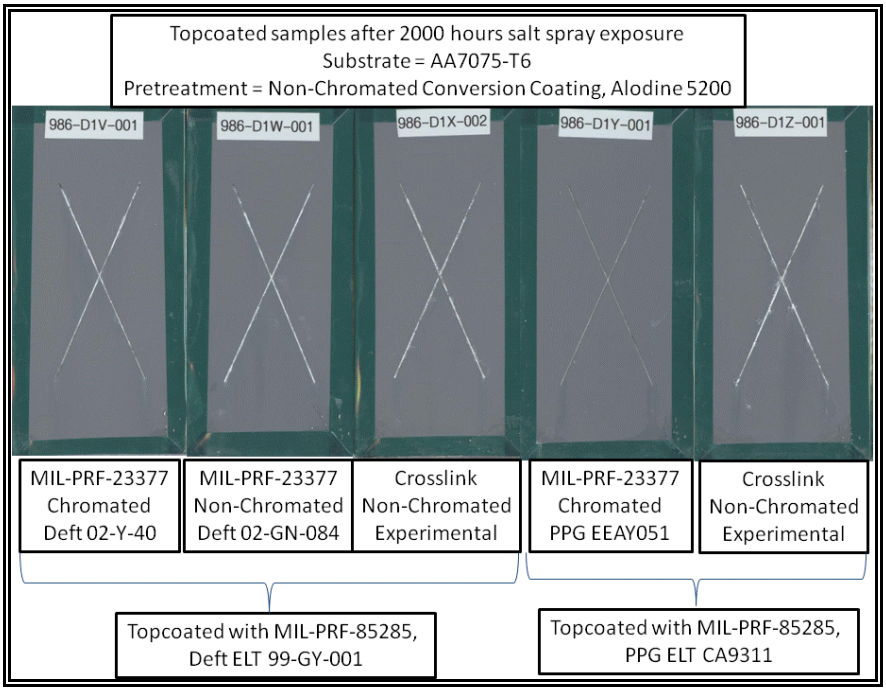



**Figure 25**: Topcoated Salt Spray Samples on AA7075-T6 after 2000 hours of Exposure: Pretreatment, Non-Chromated Conversion Coating, Alodine 5200

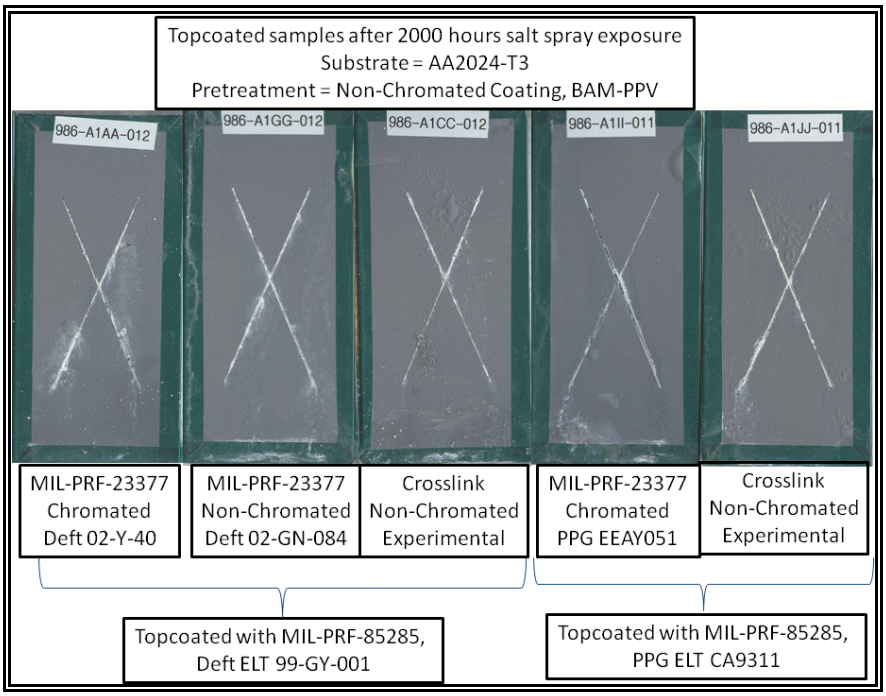



**Figure 26**: Topcoated Salt Spray Samples on AA2024-T3 after 2000 hours of Exposure: Pretreatment, Non-Chromated Coating, BAM-PPV

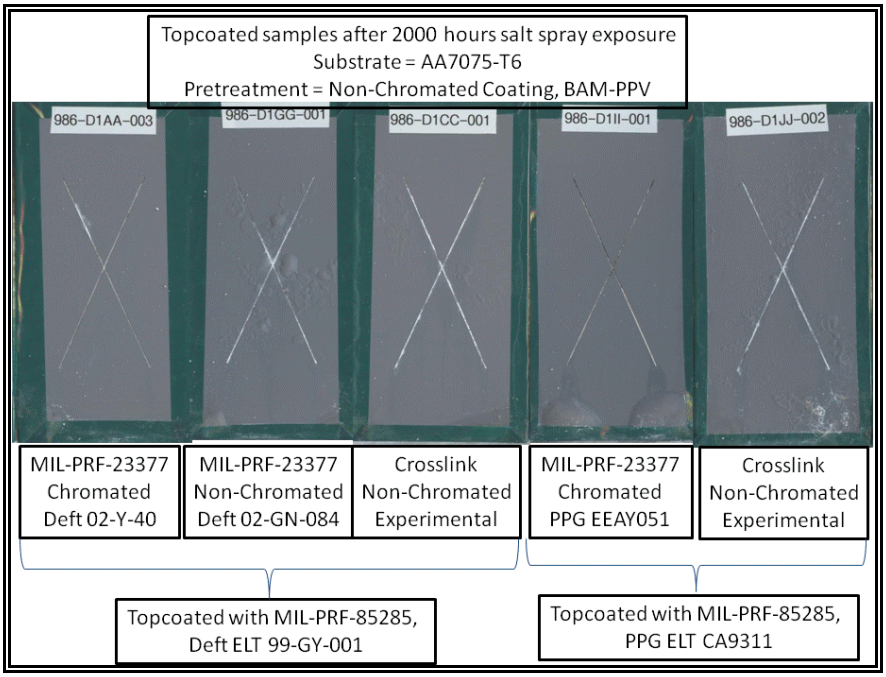



**Figure 27**: Topcoated Salt Spray Samples on AA7075-T6 after 2000 hours of Exposure: Pretreatment, Non-Chromated Coating, BAM-PPV

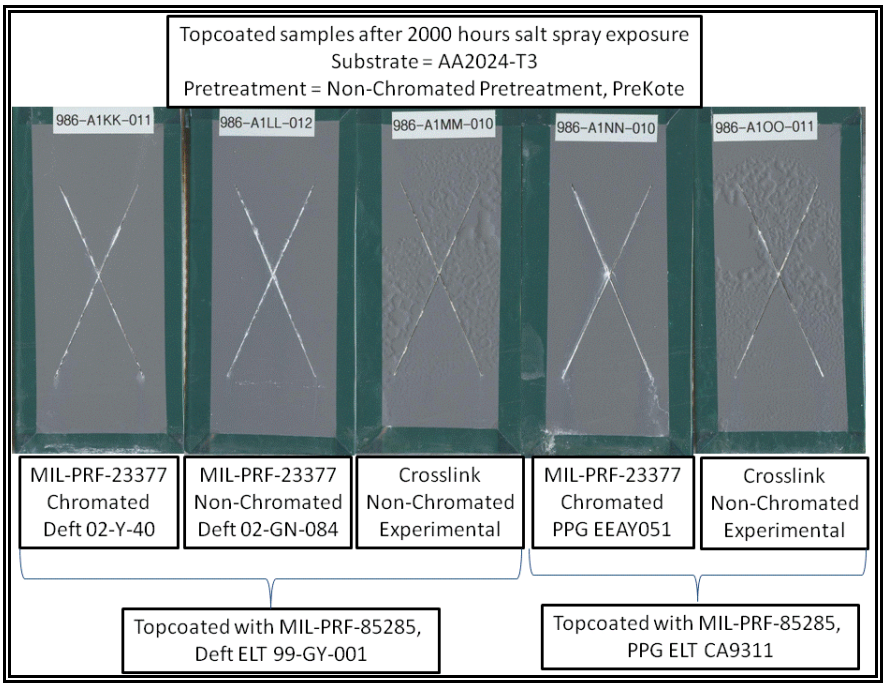



**Figure 28**: Topcoated Salt Spray Samples on AA2024-T3 after 2000 hours of Exposure: Pretreatment, Non-Chromated Surface Pretreament, PreKote

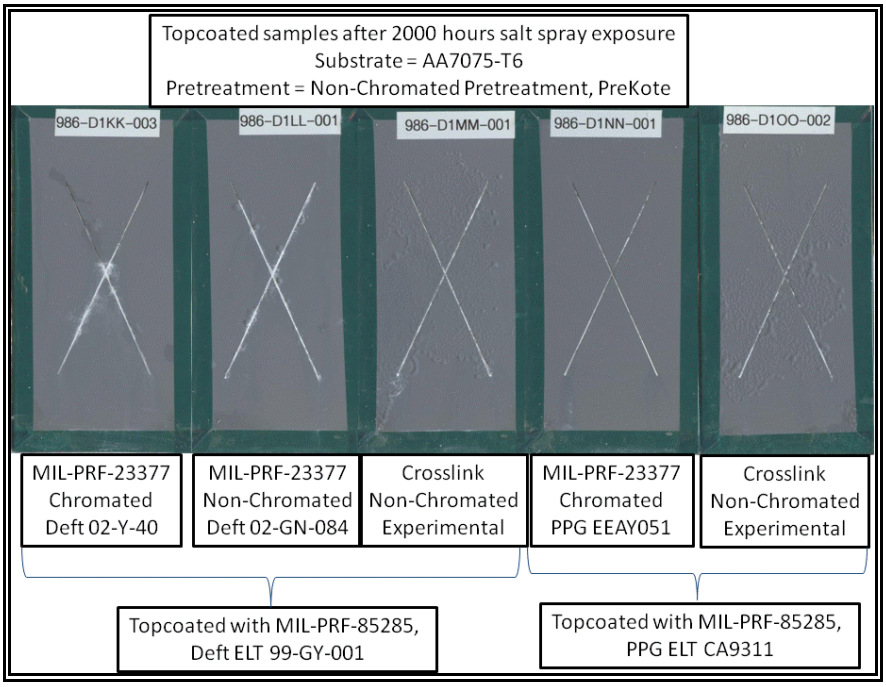



**Figure 29**: Topcoated Salt Spray Samples on AA7075-T6 after 2000 hours of Exposure: Pretreatment, Non-Chromated Surface Pretreatment, PreKote

The results from 2000 hours of NSS exposure identified that, regardless of pretreatment, the best performance in primer-only samples was seen with Cr(VI) primer systems. Additionally, in topcoated systems, the best performance was seen with Cr(VI) primers and the worst performers were non-chromated primers. These results demonstrated the continued issue with removal of chromates from the coating system. Historical testing on similar coating systems which was performed at CTIO has demonstrated that, when chromates are to be removed somewhere from the coating system (i.e., from the pretreatment or the primer), the better salt spray test performers are seen with chromate removal from the pretreatment (*Non-chromate Pretreatments versus Non-chromate Primers, Final Report*, UDRI-2187-F2-02, March 2003). It is possible that the data in the current study are reflecting similar results. Test results also showed that the BAM-PPV material supplied for testing was inconsistent with the material received for previous NSS work. Discussions with the NAWCWD and samples returned for analysis determined that the BAM-PPV molecular weight of the polymer was too high in the batch received for testing. To determine if this caused the poor results for systems where BAM-PPV was combined with the Crosslink corrosion-inhibiting primer in salt spray testing, additional samples were prepared and exposed for 500 hours. The data was then compared with the data from the previous testing at 500 hours of exposure. Results demonstrated that the BAM-PPV material performed as expected in the second round of salt spray testing, and the molecular weight and spray-ability of the material was comparable to material previously received for testing in other programs. However, the results showed that the Crosslink corrosion-inhibiting primer did not perform any better in the second round of testing, and testing was suspended after 500 hours. The data suggest that, despite the change in molecular weight to the BAM-PPV material, the Crosslink corrosion-inhibiting primer continued to demonstrate poor corrosion resistance when combined with the BAM-PPV pretreatment. It is possible that this is a formulation issue related to incompatibility with the BAM-PPV material. When the performance of the Crosslink primer is compared to that of other military specification non-chromated primers, the poor performance of the Crosslink material demonstrated that the Crosslink corrosion-inhibiting primer does not have sufficient corrosion resistance characteristics to compete. Again, this may be solved by formulation changes to the Crosslink corrosion-inhibiting primer to allow for better corrosion resistance and the data from these results are shown in Tables 22-23 and was photo-documented which are shown in Figures 30-33.

**Table 22**: Primer-Only Salt Spray Ratings (500 hours) (Repeated Testing)

| Coating System | Rating |
|---|---|
| **Pretreatment + Primer** | **AA 2024-T3 Data** |
| **Alodine 1600 + MIL-PRF-23377, chromated, Deft 02-Y-40** | **control 0 0 0** |
| Alodine 1600 + MIL-PRF-23377, non-chromated, Deft 02-GN-084 | **acceptable 2 0 0** |
| Alodine 1600 + Crosslink primer | **acceptable 0 0 0** |
| BAMPPV + MIL-PRF-23377, chromated, Deft 02-Y-40 | **acceptable 0 0 0** |
| BAMPPV + MIL-PRF-23377, non-chromated, Deft 02-GN-084 | low 1 1 0 |
| BAMPPV + Crosslink primer | **poor 0 2 0** |

**Table 23**: Salt Spray Ratings (500 hours) (MIL-PRF-85285 Topcoated Systems) (Repeated Testing)

| Coating System | Rating |
|---|---|
| **Pretreatment + Primer + Topcoat** | **AA 2024-T3 Data** |
| **Alodine 1600 + MIL-PRF-23377, chromated, Deft 02-Y-40 + MIL-PRF-85285, Deft ELT, 99-GY-001** | **control 2 0 0** |
| Alodine 1600 + MIL-PRF-23377, non-chromated, Deft 02-GN-084 + MIL-PRF-85285, Deft ELT, 99-GY-001 | **acceptable 2 0 0** |
| Alodine 1600 + Crosslink primer + MIL-PRF-85285, Deft ELT, 99-GY-001 | **acceptable 2 0 0** |
| BAMPPV + MIL-PRF-23377, chromated, Deft 02-Y-40 + MIL-PRF-85285, Deft ELT, 99-GY-001 | **acceptable 1 0 0** |
| BAMPPV + MIL-PRF-23377, non-chromated, Deft 02-GN-084 + MIL-PRF-85285, Deft ELT, 99-GY-001 | **poor 2 3 0** |
| BAMPPV + Crosslink primer + MIL-PRF-85285, Deft ELT, 99-GY-001 | **poor 2 4 0** |

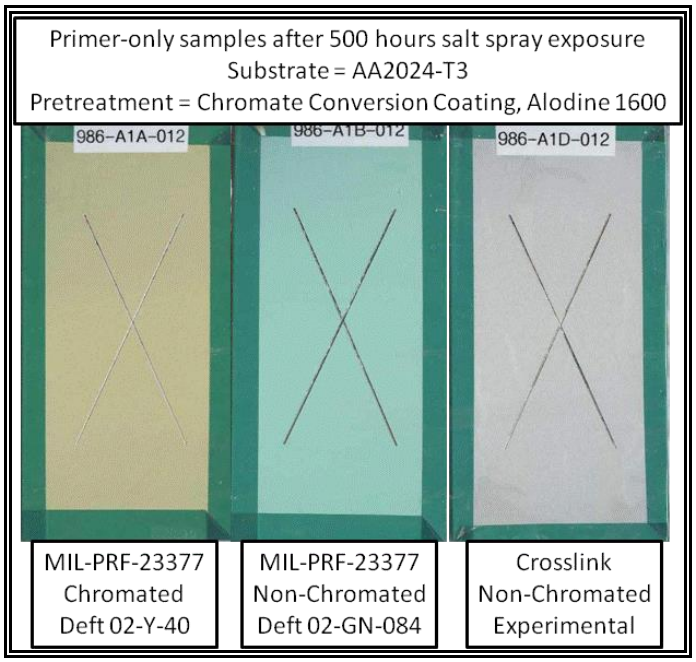



**Figure 30**: Primer-Only Salt Spray Samples on AA2024-T3 after 500 hours of Exposure: Pretreatment, Chromated Conversion Coating, Alodine 1600 (Repeated Testing)

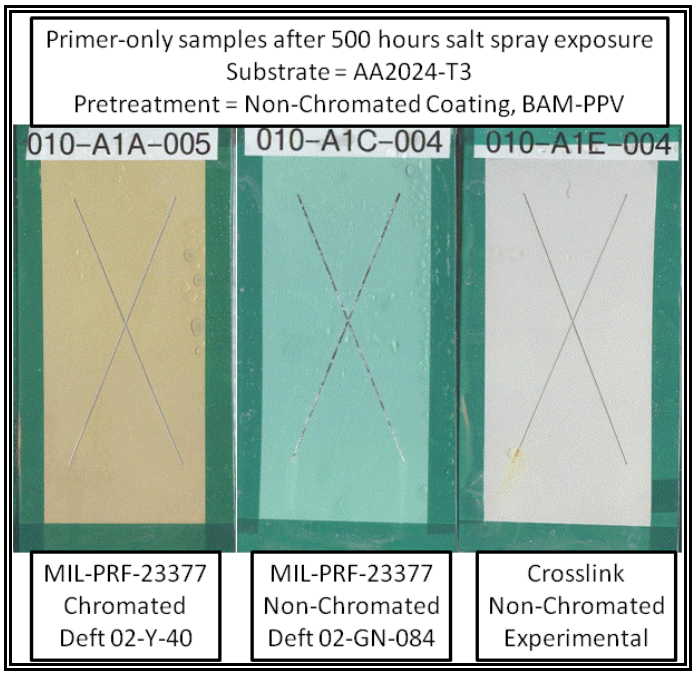



**Figure 31**: Primer-Only Salt Spray Samples on AA2024-T3 after 500 hours of Exposure: Pretreatment, Non-Chromated Coating, BAM-PPV (Repeated Testing)

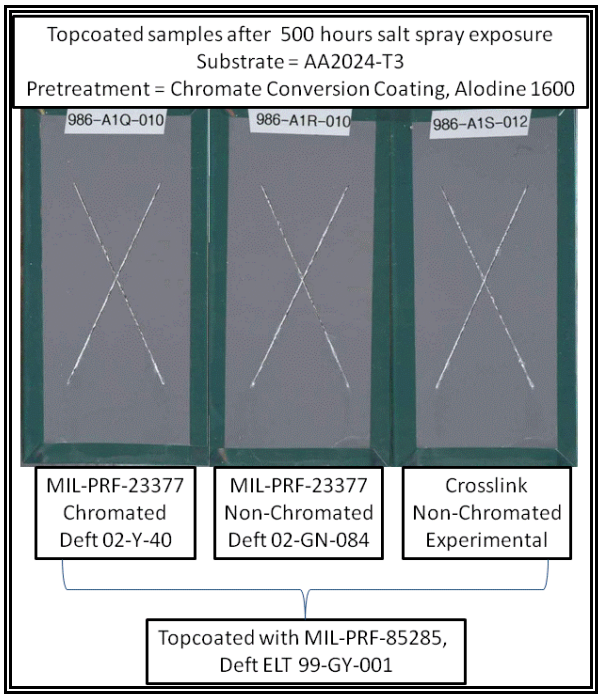



**Figure 32**: Topcoated Salt Spray Samples on AA2024-T3 after 500 hours of Exposure: Pretreatment, Chromated Conversion Coating, Alodine 1600 (Repeated Testing)

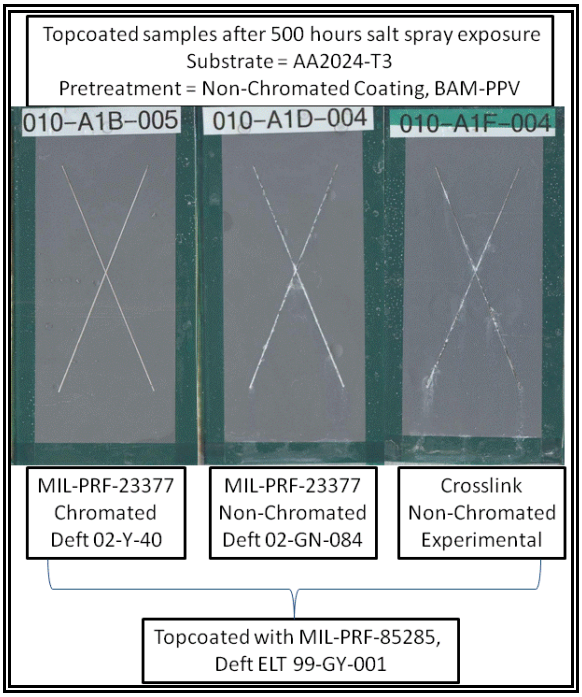



**Figure 33**: Topcoated Salt Spray Samples on AA2024-T3 after 500 hours of Exposure: Pretreatment, Non-Chromated Coating, BAM-PPV (Repeated Testing)

#### 4.1.1.3.2 GM9540P Accelerated Corrosion Test

GM9540P is an accelerated corrosion test developed by General Motors that was designed for the evaluation of assemblies and components. The procedure followed by CTIO is an adaptation of that procedure that follows the exposure cycles but does not follow specimen design or require mass loss data analysis. This method is the preferred method for accelerated corrosion testing of steel substrates and has historically provided a better comparison between laboratory-generated corrosion on steel and real-world corrosion phenomena on steel than either ASTM B 117 or ASTM G 85, *Standard Practice for Modified Salt Spray (Fog) Testing*. The data are shown in Tables 24-27. The control system is highlighted in **green**. Ratings designating acceptable performance are highlighted in **blue**. Ratings that are cause for rejection of the coating system are highlighted in **red**. Photographs of coating system behavior in GM9540P exposure are in Figures 34-45. The data suggest that there was poor corrosion control provided by the BAM-PPV and by the Crosslink materials. This was observed for systems that contained only the BAM-PPV or Crosslink corrosion-inhibiting primer along with military specification materials and for systems that contained BAM-PPV combined with the Crosslink corrosion-inhibiting primer. These results are similar to the results noted in NSS testing previously cited in this ESTCP report. It is likely that the reasons for the poor corrosion control in both of these tests are similar due to incompatibility and solvent preparation differences.

**Table 24**: GM9540P Accelerated Corrosion on 4130N Steel, Solvent-Cleaned Samples (Primer-Only Systems)

| Coating System (No Topcoat) | Rating | | | |
|---|---|---|---|---|
| **Pretreatment + Primer** | **CTIO System** | **ASTM D 1654** | **ASTM D 610** | **ASTM D 714** |
| **Cadmium Plated + MIL-PRF-23377, chromated, Deft 02-Y-40** | **control 0 0** | **control 10** | **control 10** | **control 10** |
| Cadmium Plated + MIL-PRF-23377, non-chromated, Deft 02-GN-084 | **acceptable 2 0** | **acceptable 9** | **acceptable 9S** | **acceptable 10** |
| Cadmium Plated + MIL-PRF-23377, chromated, PPG, EEAY051 | **acceptable 0 0** | **acceptable 10** | **acceptable 9S** | **acceptable 10** |
| Cadmium Plated + Crosslink primer | **acceptable 0 0** | **acceptable 10** | **acceptable 9S** | **acceptable 10** |
| No Pretreatment + MIL-PRF-23377, chromated, Deft 02-Y-40 | **poor 4 3 (M)** | **poor 3** | **poor 4G** | **poor 4 medium** |
| No Pretreatment + MIL-PRF-23377, non-chromated, Deft 02-GN-084 | **poor (completely rusted)** | **poor 0** | **poor 0** | **poor 6 dense** |
| No Pretreatment + MIL-PRF-23377, chromated, PPG, EEAY051 | **poor 4 3 (M)** | **poor 3** | **poor 6** | **poor 4 medium** |
| No Pretreatment + Crosslink primer | **poor (completely rusted)** | **poor 0** | **poor 0** | **poor 0** |
| BAMPPV + MIL-PRF-23377, chromated, Deft 02-Y-40 | **poor 4 0** | **poor 3** | **acceptable 9S** | **acceptable 10** |
| BAMPPV + MIL-PRF-23377, non-chromated, Deft 02-GN-084 | **poor 5 5 (D)** | **poor 1** | **poor 1P / 3G** | **poor 2 dense** |
| BAMPPV + MIL-PRF-23377, chromated, PPG, EEAY051 | **poor 5 4 (F)** | **poor 1** | **poor 4G** | **poor 4 few** |
| BAMPPV + Crosslink primer | **poor (completely rusted)** | **poor 0** | **poor 0** | **poor 0** |

**Table 25**: GM9540P Accelerated Corrosion on 4130N Steel, Solvent-Cleaned Samples (MIL-PRF-85285 Topcoated Systems)

| Coating System | Rating | | | |
|---|---|---|---|---|
| **Pretreatment + Primer + Topcoat** | **CTIO System** | **ASTM D 1654** | **ASTM D 610** | **ASTM D 714** |
| **Cadmium Plated + MIL-PRF-23377, chromated, Deft 02-Y-40 +** MIL-PRF-85285, Deft ELT, 99-GY-001 | **control 0 0** | **control 10** | **control 9S** | **control 10** |
| Cadmium Plated + MIL-PRF-23377, non-chromated, Deft 02-GN-084 + MIL-PRF-85285, Deft ELT, 99-GY-001 | **acceptable 1 0** | **acceptable 9** | **acceptable 9S** | **acceptable 10** |
| Cadmium Plated + Crosslink primer + MIL-PRF-85285, Deft ELT, 99-GY-001 | low 0 1 (D) | **acceptable 10** | **acceptable 9S** | low 8 dense |
| Cadmium Plated + MIL-PRF-23377, chromated, PPG, EEAY051 + MIL-PRF-85285, PPG ELT, CA9311 | **acceptable 1 0** | low 7 | **acceptable 9S** | **acceptable 10** |
| Cadmium Plated + Crosslink primer + MIL-PRF-85285, PPG ELT, CA9311 | **acceptable 1 0** | low 7 | **acceptable 9S** | **acceptable 10** |
| No Pretreatment + MIL-PRF-23377, chromated, Deft 02-Y-40 + MIL-PRF-85285, Deft ELT, 99-GY-001 | **poor 5 0** | **poor 1** | **acceptable 9S** | **acceptable 10** |
| No Pretreatment + MIL-PRF-23377, non-chromated, Deft 02-GN-084 + MIL-PRF-85285, Deft ELT, 99-GY-001 | **poor 5 0** | **poor 6** | **acceptable 9S** | **acceptable 10** |
| No Pretreatment + Crosslink primer + MIL-PRF-85285, Deft ELT, 99-GY-001 | **poor 4 3 (D)** | **poor 3** | **poor 9S** | **poor 4 dense** |
| No Pretreatment + MIL-PRF-23377, chromated, PPG, EEAY051 + MIL-PRF-85285, PPG ELT, CA9311 | **poor 3 0** | **poor 5** | **acceptable 9S** | **acceptable 10** |
| No Pretreatment + Crosslink primer + MIL-PRF-85285, PPG ELT, CA9311 | **poor 4 2 (D)** | **poor 3** | **acceptable 9S** | **poor 2 dense** |
| BAMPPV + MIL-PRF-23377, chromated, Deft 02-Y-40 + | **poor** | **poor** | **acceptable** | **acceptable** |

| | | | | |
|---|---|---|---|---|
| MIL-PRF-85285, Deft ELT, 99-GY-001 | 4 0 | 3 | 9S | 10 |
| BAMPPV +<br>MIL-PRF-23377, non-chromated, Deft 02-GN-084 +<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | poor<br>5 0 | poor<br>3 | poor<br>5G | acceptable<br>10 |
| BAMPPV +<br>Crosslink primer +<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | poor<br>5 3 (D) | poor<br>1 | acceptable<br>9S | poor<br>6 dense |
| BAMPPV +<br>MIL-PRF-23377, chromated, PPG, EEAY051 +<br>MIL-PRF-85285, PPG ELT, CA9311 | poor<br>5 0 | poor<br>1 | poor<br>5G | acceptable<br>10 |
| BAMPPV +<br>Crosslink primer +<br>MIL-PRF-85285, PPG ELT, CA9311 | poor<br>4 0 | poor<br>3 | acceptable<br>9S | acceptable<br>10 |

**Table 26**: GM9540P Accelerated Corrosion on 1010 Cold-Rolled Steel, Solvent-Cleaned Samples (Primer-Only Systems)

| **Coating System (No Topcoat)** | **Rating** | | | |
|---|---|---|---|---|
| **Pretreatment +<br>Primer** | **CTIO System** | **ASTM D 1654** | **ASTM D 610** | **ASTM D 714** |
| **Cadmium Plated +<br>MIL-PRF-23377, chromated, Deft 02-Y-40** | **control<br>0 0** | **control<br>10** | **control<br>10** | **control<br>delamination** |
| Cadmium Plated +<br>MIL-PRF-23377, non-chromated, Deft 02-GN-084 | low<br>3 0 | **acceptable<br>9** | **acceptable<br>9S** | low<br>delamination |
| Cadmium Plated +<br>MIL-PRF-23377, chromated, PPG, EEAY051 | **acceptable<br>1 0** | **acceptable<br>8** | **acceptable<br>9S** | **acceptable<br>10** |
| Cadmium Plated +<br>Crosslink primer | low<br>2 0 | low<br>6 | **acceptable<br>9S** | **acceptable<br>10** |
| No Pretreatment +<br>MIL-PRF-23377, chromated, Deft 02-Y-40 | **poor<br>3 0** | **poor<br>5** | **acceptable<br>9S** | **acceptable<br>10** |
| No Pretreatment +<br>MIL-PRF-23377, non-chromated, Deft 02-GN-084 | **poor<br>(completely<br>rusted)** | **poor<br>1** | **poor<br>0** | **poor<br>4 dense** |
| No Pretreatment +<br>MIL-PRF-23377, chromated, PPG, EEAY051 | **poor<br>4 2 (F)** | **poor<br>3** | **poor<br>5G** | low<br>8 few |
| No Pretreatment +<br>Crosslink primer | **poor<br>(completely<br>rusted)** | **poor<br>0** | **poor<br>0** | **poor<br>0** |
| BAMPPV +<br>MIL-PRF-23377, chromated, Deft 02-Y-40 | **poor<br>4 0** | **poor<br>3** | **acceptable<br>9S** | **poor<br>delamination** |
| BAMPPV +<br>MIL-PRF-23377, non-chromated, Deft 02-GN-084 | **poor<br>4 4 (MD)** | **poor<br>3** | **poor<br>4G** | **poor<br>4 medium<br>dense** |
| BAMPPV +<br>MIL-PRF-23377, chromated, PPG, EEAY051 | **poor<br>4 5 (F)** | **poor<br>3** | low<br>6S | **poor<br>2 few** |
| BAMPPV +<br>Crosslink primer | **poor<br>(completely<br>rusted)** | **poor<br>0** | **poor<br>0** | **poor<br>0** |

**Table 27**: GM9540P Accelerated Corrosion on 1010 Cold-Rolled Steel, Solvent-Cleaned Samples (MIL-PRF-85285 Topcoated Systems)

| Coating System | Rating | | | |
|---|---|---|---|---|
| **Pretreatment + Primer + Topcoat** | **CTIO System** | **ASTM D 1654** | **ASTM D 610** | **ASTM D 714** |
| **Cadmium Plated + MIL-PRF-23377, chromated, Deft 02-Y-40 +** MIL-PRF-85285, Deft ELT, 99-GY-001 | **control 0 0** | **control 10** | **control 10** | **control 10** |
| Cadmium Plated + MIL-PRF-23377, non-chromated, Deft 02-GN-084 + MIL-PRF-85285, Deft ELT, 99-GY-001 | low 2 0 | low 6 | **acceptable 9S** | **acceptable 10** |
| Cadmium Plated + Crosslink primer + MIL-PRF-85285, Deft ELT, 99-GY-001 | low 2 1 (D) | low 6 | **acceptable 9S** | low 8 dense |
| Cadmium Plated + MIL-PRF-23377, chromated, PPG, EEAY051 + MIL-PRF-85285, PPG ELT, CA9311 | **acceptable 0 0** | **acceptable 10** | **acceptable 10** | **acceptable 10** |
| Cadmium Plated + Crosslink primer + MIL-PRF-85285, PPG ELT, CA9311 | low 2 0 | low 6 | **acceptable 9S** | **acceptable 10** |
| No Pretreatment + MIL-PRF-23377, chromated, Deft 02-Y-40 + MIL-PRF-85285, Deft ELT, 99-GY-001 | **poor 4 0** | **poor 3** | **acceptable 9S** | **acceptable 10** |
| No Pretreatment + MIL-PRF-23377, non-chromated, Deft 02-GN-084 + MIL-PRF-85285, Deft ELT, 99-GY-001 | **poor 4 0** | **poor 3** | **acceptable 9S** | **acceptable 10** |
| No Pretreatment + Crosslink primer + MIL-PRF-85285, Deft ELT, 99-GY-001 | **poor 5 0** | **poor 1** | **acceptable 9S** | **acceptable 10** |
| No Pretreatment + MIL-PRF-23377, chromated, PPG, EEAY051 + MIL-PRF-85285, PPG ELT, CA9311 | **poor3 0** | **poor 5** | **acceptable 9S** | **acceptable 10** |
| No Pretreatment + Crosslink primer + MIL-PRF-85285, PPG ELT, CA9311 | **poor 4 0** | **poor 3** | **acceptable 9S** | **acceptable 10** |
| BAMPPV + MIL-PRF-23377, chromated, Deft 02-Y-40 + MIL-PRF-85285, Deft ELT, 99-GY-001 | **poor 4 0** | **poor 1** | **acceptable 9S** | **acceptable 10** |
| BAMPPV + MIL-PRF-23377, non-chromated, Deft 02-GN-084 + MIL-PRF-85285, Deft ELT, 99-GY-001 | **poor 5 0** | **poor 1** | **acceptable 9S** | **acceptable 10** |
| BAMPPV + Crosslink primer + MIL-PRF-85285, Deft ELT, 99-GY-001 | **poor 5 3 (D)** | **poor 1** | **acceptable 9S** | **poor 6 dense** |
| BAMPPV + MIL-PRF-23377, chromated, PPG, EEAY051 + MIL-PRF-85285, PPG ELT, CA9311 | **poor 5 0** | **poor 1** | **acceptable 9S** | **acceptable 10** |
| BAMPPV + Crosslink primer + MIL-PRF-85285, PPG ELT, CA9311 | low 3 0 | **poor 5** | **acceptable 9S** | **acceptable 10** |

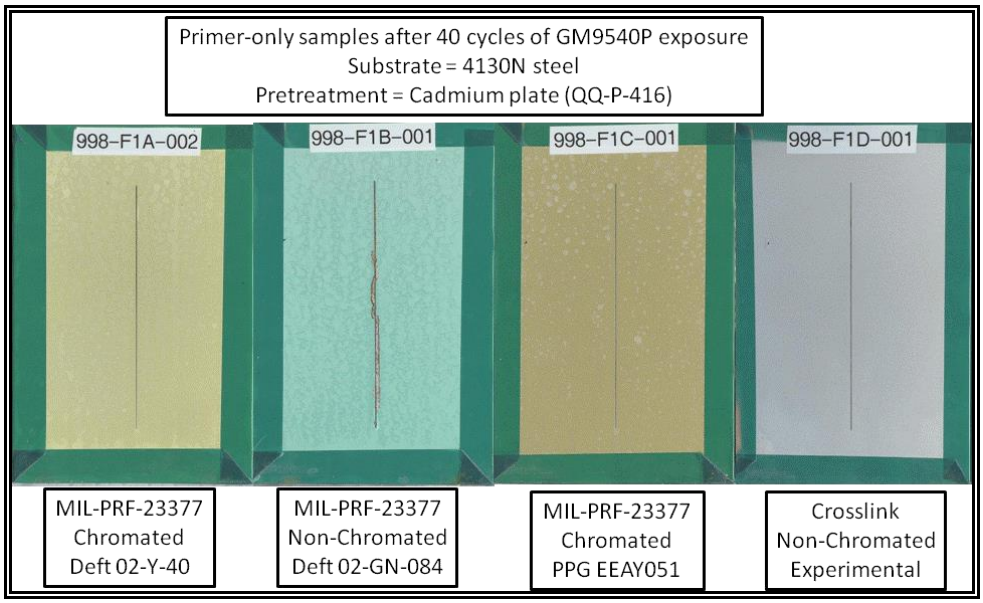



**Figure 34**: Primer-Only Samples on 4130N steel after 40 cycles of GM9540P Exposure: Pretreatment, Cadmium Plate per QQ-P-416

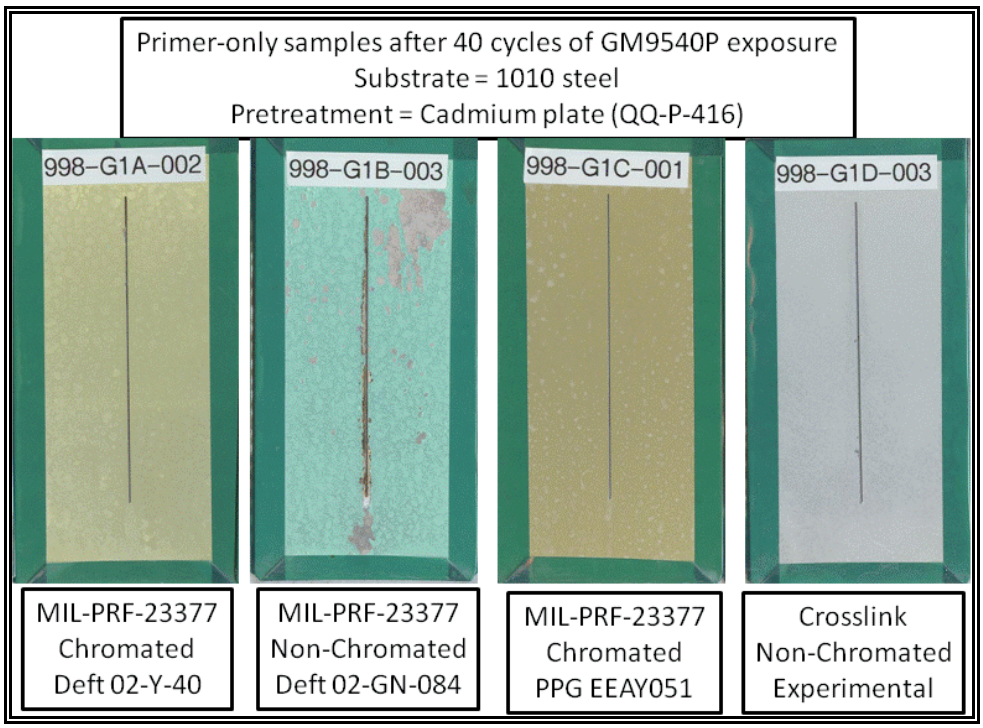



**Figure 35**: Primer-Only Samples on 1010 steel after 40 cycles of GM9540P Exposure: Pretreatment, Cadmium Plate per QQ-P-416

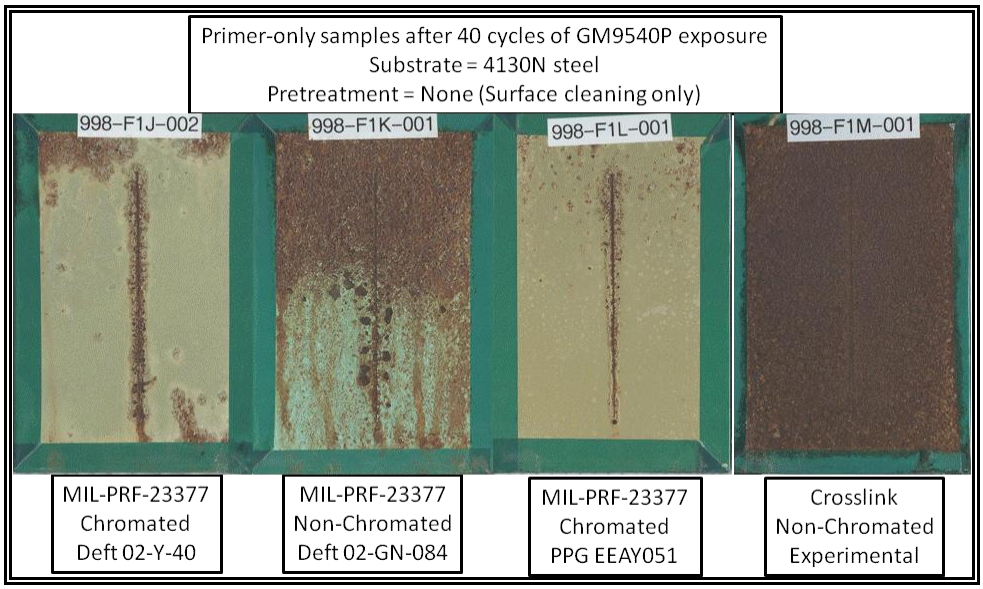



**Figure 36**: Primer-Only Samples on 4130N steel after 40 cycles of GM9540P Exposure: No Pretreatment, Surface Cleaning Only

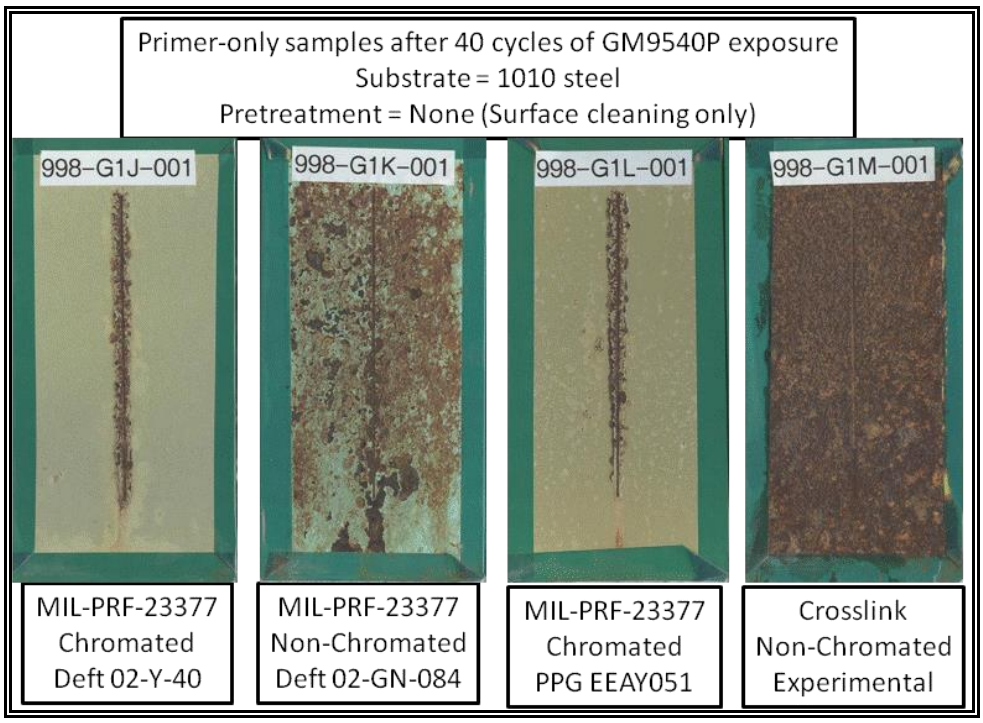



**Figure 37**: Primer-Only Samples on 1010 steel after 40 cycles of GM9540P Exposure: No Pretreatment, Surface Cleaning Only

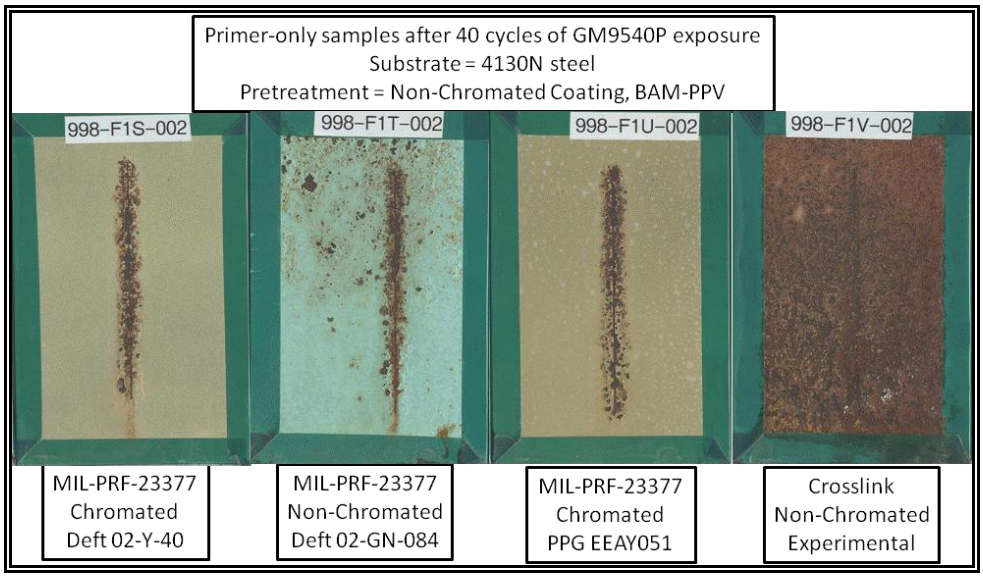



**Figure 38**: Primer-Only Samples on 4130N steel after 40 cycles of GM9540P Exposure: Pretreatment, Non-Chromated Coating, BAM-PPV

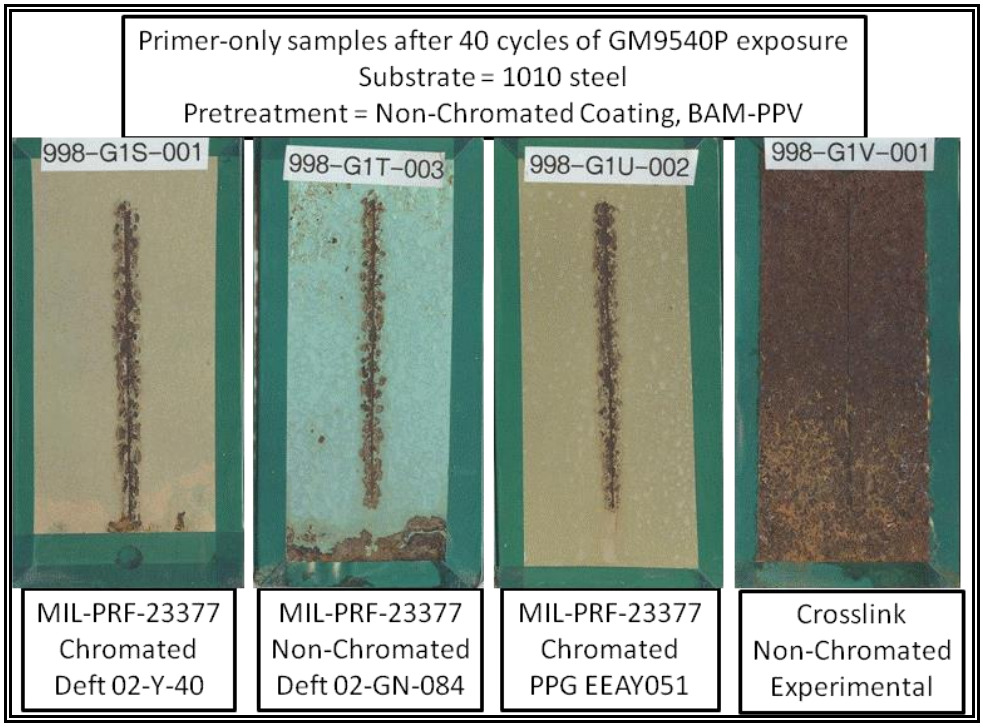



**Figure 39**: Primer-Only Samples on 1010 steel after 40 cycles of GM9540P Exposure: Pretreatment, Non-Chromated Coating, BAM-PPV

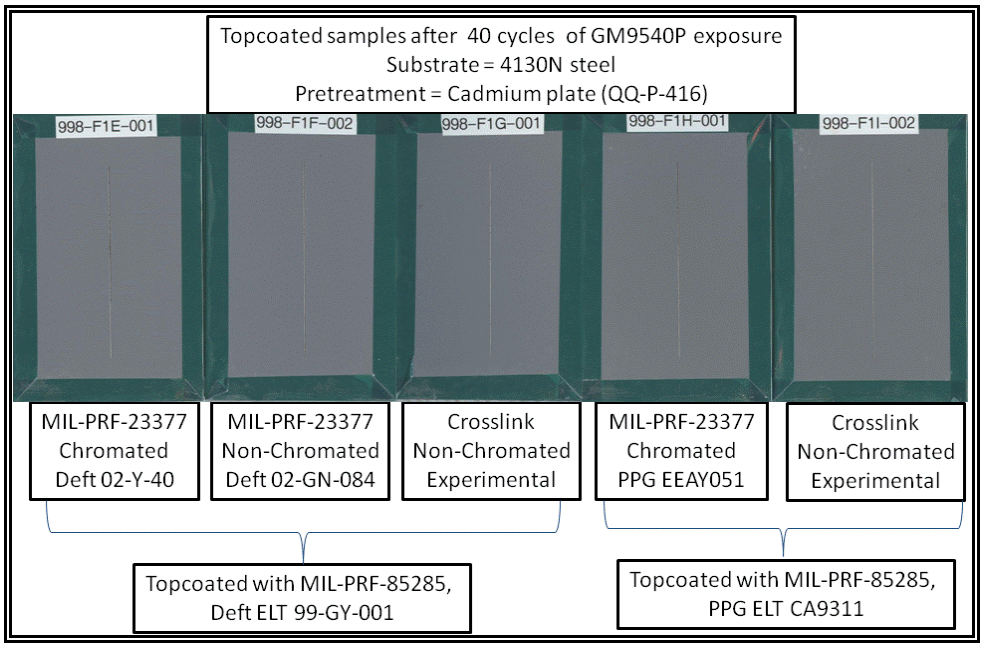



**Figure 40**: Topcoated Samples on 4130N steel after 40 cycles of GM9540P Exposure: Pretreatment, Cadmium Plate per QQ-P-416

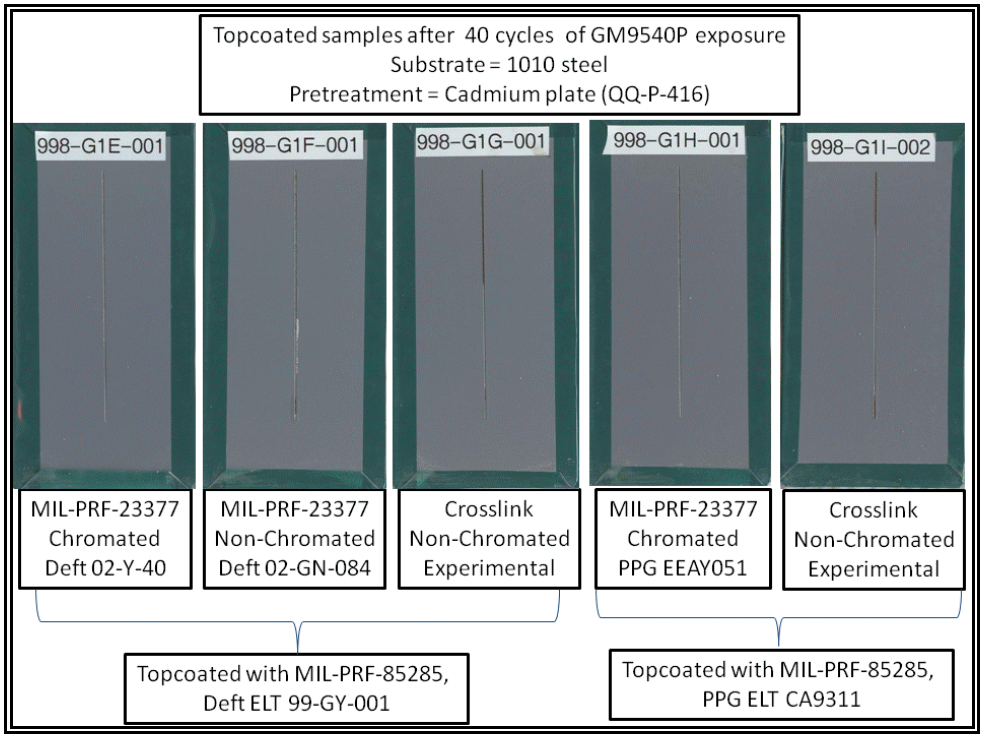



**Figure 41**: Topcoated Samples on 1010 steel after 40 cycles of GM9540P Exposure: Pretreatment, Cadmium Plate per QQ-P-416

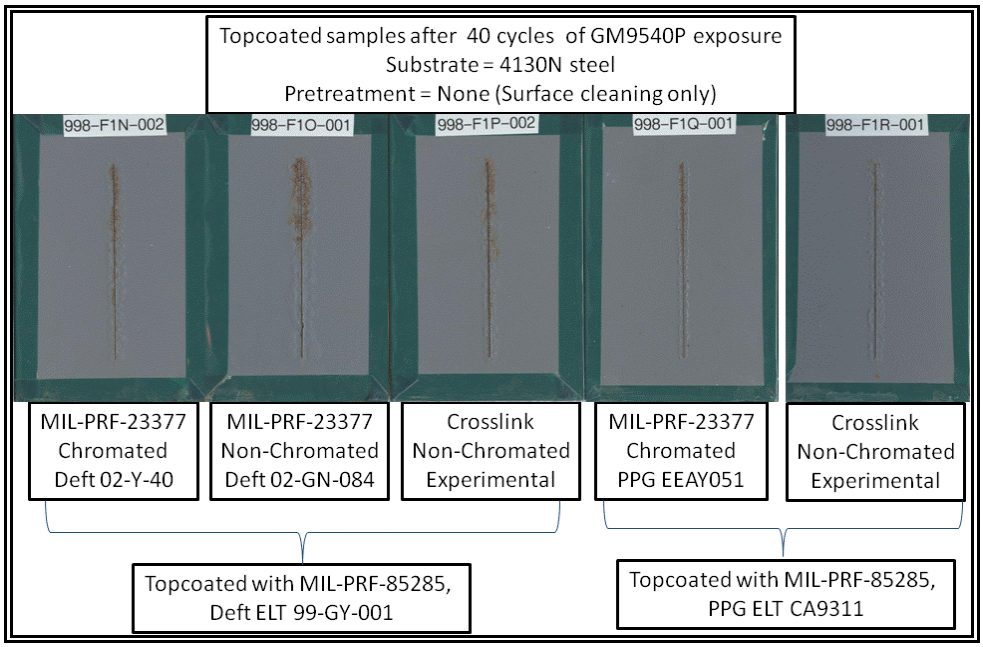



**Figure 42**: Topcoated Samples on 4130N steel after 40 cycles of GM9540P Exposure: No Pretreatment (Surface Cleaning Only)

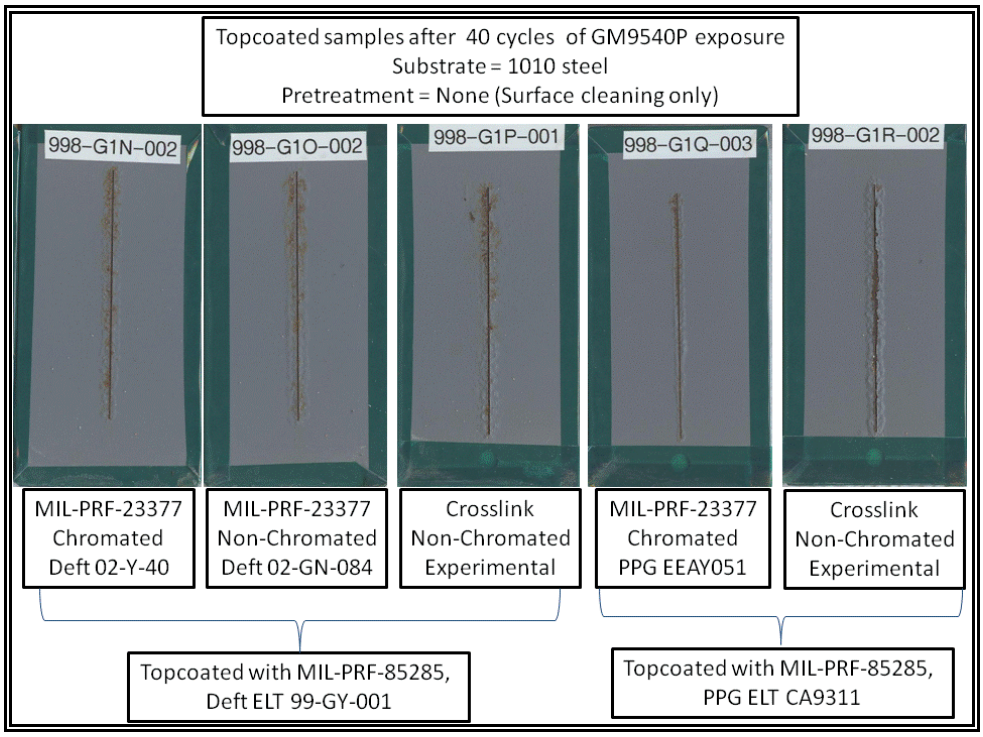



**Figure 43**: Topcoated Samples on 1010 steel after 40 cycles of GM9540P Exposure: No Pretreatment (Surface Cleaning Only)

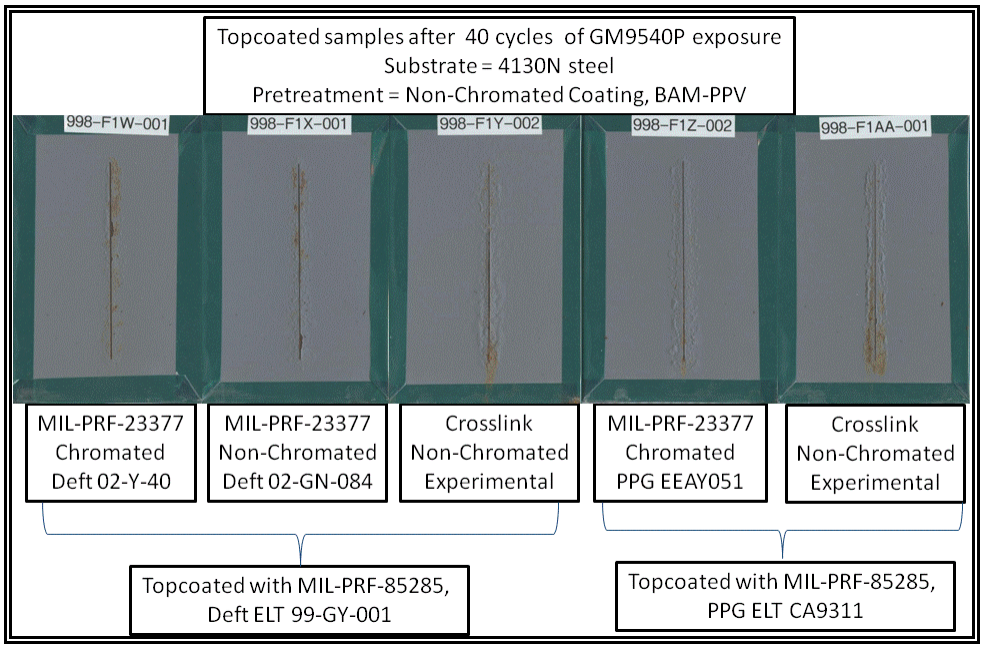



**Figure 44**: Topcoated Samples on 4130N steel after 40 cycles of GM9540P Exposure: Pretreatment, Non-Chromated Coating, BAM-PPV

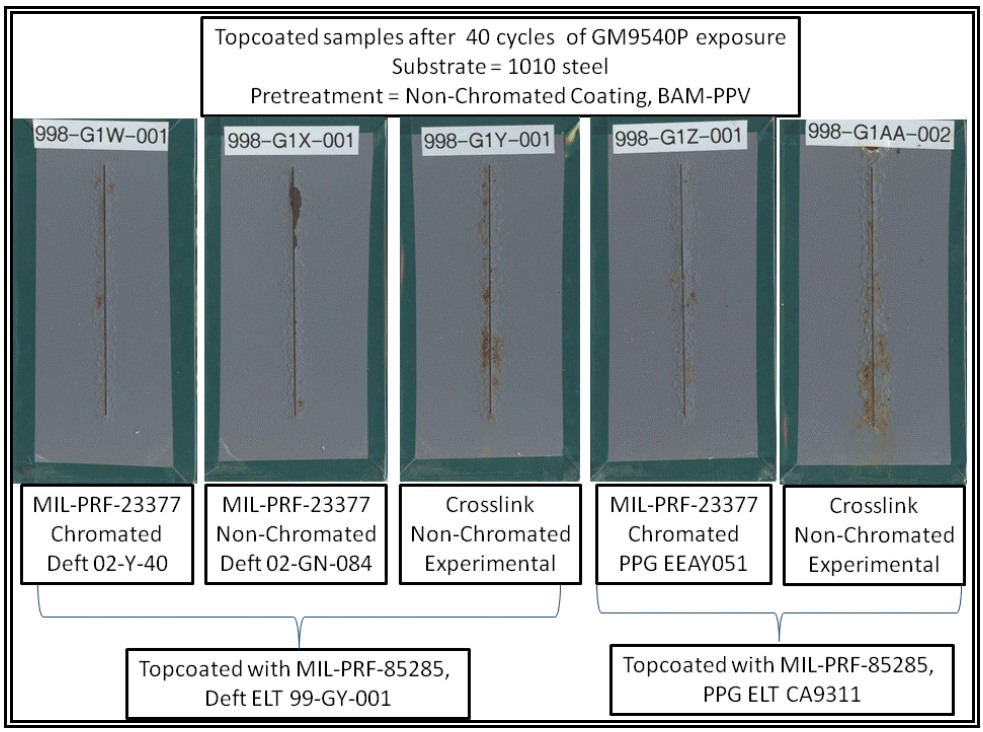



**Figure 45**: Topcoated Samples on 1010 steel after 40 cycles of GM9540P Exposure: Pretreatment, Non-Chromated Coating, BAM-PPV

#### 4.1.1.4 Additional Testing of Crosslink Primer Systems

##### 4.1.1.4.1 ASTM D 3363 Pencil Hardness

This test follows ASTM D 3363 and provides a rapid determination of the hardness of the Crosslink primer coating systems. The data that were obtained are comparative in nature. This means that the behavior of the control system is often used as a metric for the rating of the remaining systems. Often, topcoat ratings which fall within B through 2H are considered "acceptable", but this can vary based upon the type of the coating system. Primer ratings are often one or two grades harder. This test was performed on (*i*) primed and (*ii*) topcoated systems. The results from this test are found in Tables 28-29. Ratings that are considered "acceptable" are highlighted in **blue**. Ratings that are outside of the typical "acceptable" range are highlighted in **red**. The control system is highlighted in **green**.

**Table 28**: ASTM D 3363 Pencil Hardness (Primed Systems)

| **Coating System (No Topcoat)** | **Rating** |
|---|---|
| **Pretreatment + Primer** | **AA 2024-T3 Data** |
| **Alodine 1600 + MIL-PRF-23377, chromated, Deft 02-Y-40** | **control F** |
| Alodine 1600 + MIL-PRF-23377, non-chromated, Deft 02-GN-084 | **2H** |
| Alodine 1600 + MIL-PRF-23377, chromated, PPG, EEAY051 | **F** |
| Alodine 1600 + Crosslink primer | **F** |
| Alodine 5200 + MIL-PRF-23377, chromated, Deft 02-Y-40 | **F** |
| Alodine 5200 + MIL-PRF-23377, non-chromated, Deft 02-GN-084 | **3H** |
| Alodine 5200 + MIL-PRF-23377, chromated, PPG, EEAY051 | **3H** |
| Alodine 5200 + Crosslink primer | **2H** |
| BAMPPV + MIL-PRF-23377, chromated, Deft 02-Y-40 | **F** |
| BAMPPV + MIL-PRF-23377, non-chromated, Deft 02-GN-084 | **F** |
| BAMPPV + MIL-PRF-23377, chromated, PPG, EEAY051 | **F** |
| BAMPPV + Crosslink primer | **2H** |
| Prekote + MIL-PRF-23377, chromated, Deft 02-Y-40 | **2H** |
| Prekote + MIL-PRF-23377, non-chromated, Deft 02-GN-084 | **H** |

| | |
|---|---|
| Prekote +<br>MIL-PRF-23377, chromated, PPG, EEAY051 | **3H** |
| Prekote +<br>Crosslink primer | **2H** |

**Table 29**: ASTM D 3363 Pencil Hardness (MIL-PRF-85285 Topcoated Systems)

| **Coating System** | **Rating** |
|---|---|
| **Pretreatment +<br>Primer +<br>Topcoat** | **AA 2024-T3<br>Data** |
| **Alodine 1600 +<br>MIL-PRF-23377, chromated, Deft 02-Y-40<br>MIL-PRF-85285, Deft ELT, 99-GY-001** | **control<br>B** |
| Alodine 1600 +<br>MIL-PRF-23377, non-chromated, Deft 02-GN-084<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | **F** |
| Alodine 1600 +<br>Crosslink primer +<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | **F** |
| Alodine 1600 +<br>MIL-PRF-23377, chromated, PPG, EEAY051<br>MIL-PRF-85285, PPG ELT, CA9311 | **F** |
| Alodine 1600 +<br>Crosslink primer<br>MIL-PRF-85285, PPG ELT, CA9311 | **F** |
| Alodine 5200 +<br>MIL-PRF-23377, chromated, Deft 02-Y-40<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | **HB** |
| Alodine 5200 +<br>MIL-PRF-23377, non-chromated, Deft 02-GN-084<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | **F** |
| Alodine 5200 +<br>Crosslink primer<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | **F** |
| Alodine 5200 +<br>MIL-PRF-23377, chromated, PPG, EEAY051<br>MIL-PRF-85285, PPG ELT, CA9311 | **F** |
| Alodine 5200 +<br>Crosslink primer<br>MIL-PRF-85285, PPG ELT, CA9311 | **F** |
| BAMPPV +<br>MIL-PRF-23377, chromated, Deft 02-Y-40<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | **B** |
| BAMPPV +<br>MIL-PRF-23377, non-chromated, Deft 02-GN-084<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | **F** |
| BAMPPV +<br>Crosslink primer<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | **HB** |

| | |
|---|---|
| BAMPPV +<br>MIL-PRF-23377, chromated, PPG, EEAY051<br>MIL-PRF-85285, PPG ELT, CA9311 | **B** |
| BAMPPV +<br>Crosslink primer<br>MIL-PRF-85285, PPG ELT, CA9311 | **B** |
| Prekote +<br>MIL-PRF-23377, chromated, Deft 02-Y-40<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | **HB** |
| Prekote +<br>MIL-PRF-23377, non-chromated, Deft 02-GN-084<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | **F** |
| Prekote +<br>Crosslink primer<br>MIL-PRF-85285, Deft ELT, 99-GY-001 | **F** |
| Prekote +<br>MIL-PRF-23377, chromated, PPG, EEAY051<br>MIL-PRF-85285, PPG ELT, CA9311 | **F** |
| Prekote +<br>Crosslink primer<br>MIL-PRF-85285, PPG ELT, CA9311 | **F** |

#### 4.1.1.4.2 Physical Requirement: Surface Appearance (MIL-PRF-32239)

The mil-spec MIL-PRF-32239 states that surface appearance is a requirement for applied surface coating systems. The test is visual and was applied to the Crosslink primer system coatings. The Crosslink primer after application to the substrate, cannot exhibit runs, sags, bubbles, streaks, hazing, seeding, dusting, floating, mottling, or other defects. The coating system must exhibit a uniform, smooth surface that is free from defects. The testing for this ESTCP program was focused around the compatibility of pretreatments or primers with other military pretreatments or primers, the primer-only systems were evaluated without topcoats. The results were taken 24 hours after the primers were applied and none of the primer systems (i.e., the pretreatment and primer combinations) in this study exhibited defects. All primer systems were uniform and smooth as-applied over pretreatments. All primer systems including the Crosslink primer coating received a pass rating for the surface appearance requirement.

#### 4.1.1.4.3 Physical Requirement: Odor (MIL-PRF-32239)

The mil-spec MIL-PRF-32239 states that the test for residual odor is a requirement for the admixed properties of applied surface coating systems. The test is pass/fail and is based upon the average user's sense of smell. As with the surface appearance test, because the testing in this program was focused around the compatibility of pretreatments or primers with other military pretreatments or primers, the Crosslink primer-only systems were tested. The results were taken 48 hours after the primers were applied and samples were then isolated in covered glass beakers for 20 minutes at room temperature. The cover was removed and samples were checked for the presence of odor. None of the Crosslink primer systems (i.e., the pretreatment and primer combinations) in

this study exhibited any residual odor and therefore all the Crosslink primer systems received a "pass" rating for the odor requirement.

#### 4.1.1.4.4 Physical Requirement: Drying Time (MIL-PRF-32239)

The mil-spec MIL-PRF-32239 states that all systems will be tested for drying time as a full system rather than the individual components of pretreatment, primer, and topcoat. In this test, coatings must comply with the following:

> "Coating system components designated as surface pretreatments shall be dry to prime within 4 hours. Coating system components designated as primers shall be dry to topcoat within 5 hours. Coating system components designated as topcoats shall be dry to tape with no adhesion loss or permanent marring in 8 hours or less when tested in accordance with (MIL-PRF-32239). As an alternative, the total time to apply pretreatment, primer, and topcoat to a dry to tape condition shall be 17 hours or less."

As with the surface appearance test and the odor test, the testing for this ESTCP program was focused around the compatibility of pretreatments or primers with other military pretreatments or primers and therefore the Crosslink primer–only systems were tested. Systems were checked for adhesion following the test protocol in MIL-PRF-32239. None of the primer systems (i.e., the pretreatment and primer combinations) in this study exhibited any loss of adhesion. All Crosslink primer systems received a "pass" rating for the dry-to-tape requirement.

#### 4.1.1.4.5 Reparability Testing of the Crosslink Primer System

This test was a requirement for potential field test preparation. The reparability testing focused on the behavior of the Crosslink primer coating when applied as a repair coating to an existing system. The test method assumed that the standard system found on many USAF aircraft was the MIL-DTL-81706 chromated conversion coating, MIL-PRF-23377 chromated epoxy primer, and MIL-PRF-85285 ELT. This was the system for repair of or replacement with non-chromated coatings by changing the pretreatment or pretreatment and primer in the system. For this test, coating combinations are given in Table 30. There were several alternative systems examined and are bulletized here for easy reading:

- BAM-PPV replacing the chromated conversion coating in the standard system,
- Pantheon PreKote (PreKote) replacing the chromated conversion coating in the standard system,
- BAM-PPV and non-chromated Crosslink primer replacing the chromated conversion coating and MIL-PRF-23377 chromated primer in the standard system,

- PreKote and non-chromated Crosslink primer replacing the chromated conversion coating and MIL-PRF-23377 chromated primer in the standard system,
- BAM-PPV and MIL-PRF-23377 non-chromated primer Deft 02-GN-084 replacing the chromated conversion coating and MIL-PRF-23377 chromated primer in the standard system and
- PreKote and non-chromated primer Deft 02-GN-084 replacing the chromated conversion coating and MIL-PRF-23377 chromated primer in the standard system.

**Table 30**: Reparability Testing for AA2024-T3 (Bare 0.032 inches)

| Location on 12 x 12 in. Panel | Primary Coating System | | | Repair Coating System | | |
|---|---|---|---|---|---|---|
| | Pretreatment | Primer | Topcoat | Pretreatment | Primer | Topcoat |
| Left Side | Alodine 1600 | Deft 02-Y-40A | Deft ELT 99-GY-001 | BAM-PPV | Deft 02-Y-40A | Deft ELT 99-GY-001 |
| Right Side | BAM-PPV | Deft 02-Y-40A | Deft ELT 99-GY-001 | | | |
| Left Side | Alodine 1600 | Crosslink | Deft ELT 99-GY-001 | BAM-PPV | Crosslink | Deft ELT 99-GY-001 |
| Right Side | BAM-PPV | Crosslink | Deft ELT 99-GY-001 | | | |
| Left Side | Alodine 1600 | Deft 02-Y-40A | Deft ELT 99-GY-001 | PreKote | Deft 02-Y-40A | Deft ELT 99-GY-001 |
| Right Side | PreKote | Deft 02-Y-40A | Deft ELT 99-GY-001 | | | |
| Left Side | Alodine 1600 | Crosslink | Deft ELT 99-GY-001 | PreKote | Crosslink | Deft ELT 99-GY-001 |
| Right Side | PreKote | Crosslink | Deft ELT 99-GY-001 | | | |
| Left Side | Alodine 1600 | Deft 02-Y-40A | Deft ELT 99-GY-001 | BAM-PPV | Deft 02-GN-084 | Deft ELT 99-GY-001 |
| Right Side | BAM-PPV | Deft 02-Y-40A | Deft ELT 99-GY-001 | | | |
| Left Side | Alodine 1600 | Deft 02-Y-40A | Deft ELT 99-GY-001 | PreKote | Deft 02-GN-084 | Deft ELT 99-GY-001 |

The entire alternative coating systems was top-coated with MIL-PRF-85285 ELT polyurethane Deft 99-GY-001 (color Federal Standard Color 36173). These systems were applied to AA2024-T3 bare 0.032-inch substrate sized 12 x 12 inches, cured for 14-days at ambient laboratory conditions (77°F and 50% RH), and subject to exposure, selective removal, and full recoat procedures as described in this section. The goal was to identify coating system combinations for reparability of current systems with the alternative coating systems and of an alternative system with itself.

Because of limited availability of materials and finite accelerated weathering cabinet space, each 12 x 12 inch sample had two "primary" systems applied on 6 x 12 inch portions of the sample (Figure 46).

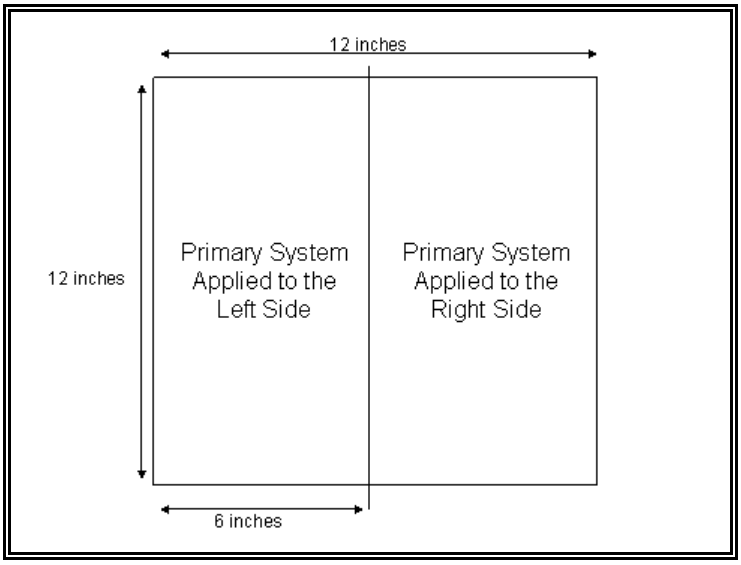



**Figure 46**: Primary Coating System Application for Reparability Samples

Prior to exposure, color and gloss data was taken on the samples following UDRI/CTIO Laboratory Procedure CLG-LP-027, *Computer Controlled Color-Gloss-DFT System*. Samples were then exposed to accelerated weathering through ultraviolet-B (UVB) exposure for 1000 hours. Operation of the exposure test followed UDRI/CTIO Laboratory Procedure CLG-LP-021 *UV Condensation Exposure* which was conducted in accordance with ASTM D 4587, *Standard Practice for Fluorescent UV-Condensation Exposures of Paint and Related Coatings*, and ASTM G 154, *Standard Practice for Operating Fluorescent Light Apparatus for UV Exposure of Nonmetallic Materials*. Color and gloss data was taken again at the 1000-hour exposure point. Each sample was then ground down using an orbital sander to remove the coating in layers so that the final result was bare substrate exposed in one band, primer exposed in one band, and topcoat exposed in the other band (approximately in thirds; Figure 47). Samples were wiped clean with isopropanol and then with methyl ethyl ketone (MEK). The repair coating system was applied to the samples as given Table 30, identified as the "repair system." The systems were applied in a stack-up, with care taken to apply pretreatment only to the bare substrate portions of the sample followed by primer and topcoat application over the entire sample. Samples cured for 14 days at standard laboratory conditions. Color and gloss data was taken and recorded as the 1000-hour post-repair point.

Samples were returned to UVB exposure for 1000 hours and removed. Color and gloss data was taken and recorded as the end-of-test point. Color data was then compared for degradation rate and verified against the requirements of MIL-PRF-32239, *Performance Specification, Coating System, Advanced Performance, For Aerospace Applications*. Those requirements are that the coating exhibit a color change ($\Delta E$) no greater than 1.0 units and that the total gloss measurement of gunship coatings be no greater than 3 units when measured at a 60° angle of incidence.

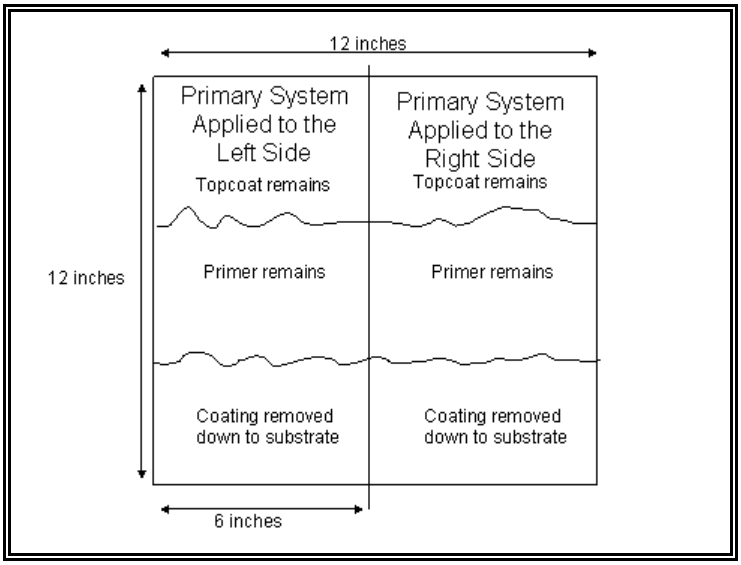



**Figure 47**: Coating System Removal for Reparability Testing

The Crosslink coating systems were then tested for adhesion and hardness characteristics post-exposure along the interfaces (Figure 48). UDRI/CTIO Laboratory Procedure CLG-LP-008 *Tape Test Adhesion* and UDRI/CTIO Laboratory Procedure CLG-LP-005 *Pencil Hardness of Coatings* were utilized to perform these tests. These procedures conformed to ASTM D 3359 *Standard Test Methods for Measuring Adhesion by Tape Test*, Method A, *X-Cut Tape Adhesion* and ASTM D 3363 *Standard Test Method for Film Hardness by Pencil Test* respectively. The data was compared to previous data from unexposed systems to provide overall information about the weathering and adhesion characteristics of the coating systems and repair systems. For adhesion testing, a "pass" rating was given to coating systems with a 4A or better result. For pencil hardness, a "pass" rating was given to coating systems with a pencil hardness rating that changed no more than 2 units from initial values.

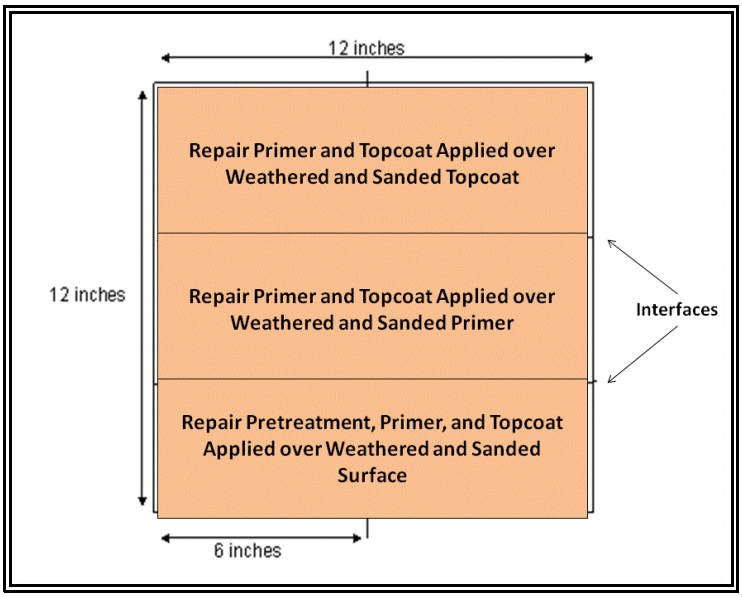



**Figure 48**: Coating System Interfaces for Adhesion Testing in the Reparability Test

Reparability testing was selected from the ESTCP proposal and from discussions between China Lake and AFRL/RXSSO CTIO. All selected tests are designed to evaluate the most pertinent coatings issues encountered with coating systems. The majority of the tests were taken from MIL-PRF-32239 that references military, federal, and technical specifications. Evaluation followed guidelines from MIL-PRF-32239.

Reparability testing focused on the behavior of the material when applied as a repair coating to an existing system. The test method assumed that the standard system found on many USAF aircraft was the MIL-DTL-81706 chromated conversion coating, MIL-PRF-23377 chromated epoxy primer, and MIL-PRF-85285 ELT. This was the system for repair of or replacement with non-chromated coatings by changing the pretreatment or pretreatment and primer in the system (See Table 30). The goal was to identify coating system combinations for reparability of current systems with the alternative coating systems and of an alternative system with itself. Samples were coated, exposed, sanded, re-coated, re-exposed, and tested. Color and gloss data was collected to compare coating system performance and repair coating system performance. At the completion of re-exposure, adhesion testing was performed as illustrated in Figure 49. Adhesion testing was performed with guidance from ASTM D 3359, Method A. Pencil hardness testing was performed in accordance with ASTM D 3363. Test results are given in Tables 31-33. Previous results for adhesion and pencil hardness for unexposed systems are given in Table 34 for comparison.

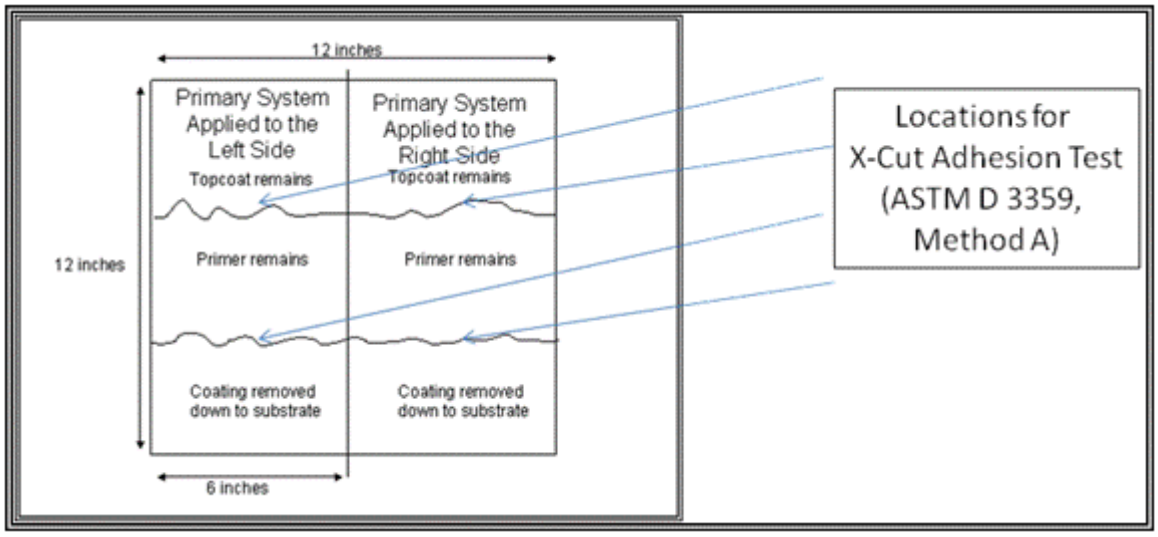



**Figure 49**: Locations for Interfaces, Adhesion Testing in the Reparability Test

**Table 31**: Reparability Results, Color Data

| Primary Coating System | | | Repair Coating System | | | 1000 hours UVB ΔE before Repair | 1000 hours UVB ΔE after Repair |
|---|---|---|---|---|---|---|---|
| **Pretreatment** | **Primer** | **Topcoat** | **Pretreatment** | **Primer** | **Topcoat** | | |
| Alodine 1600 | Deft 02-Y-40A | Deft ELT 99-GY-001 | BAM-PPV | Deft 02-Y-40A | Deft ELT 99-GY-001 | 0.53 | 0.98 |
| BAM-PPV | Deft 02-Y-40A | Deft ELT 99-GY-001 | | | | 0.34 | 0.98 |
| Alodine 1600 | Crosslink | Deft ELT 99-GY-001 | BAM-PPV | Crosslink | Deft ELT 99-GY-001 | 0.14 | 0.77 |
| BAM-PPV | Crosslink | Deft ELT 99-GY-001 | | | | 0.25 | 0.79 |
| Alodine 1600 | Deft 02-Y-40A | Deft ELT 99-GY-001 | PreKote | Deft 02-Y-40A | Deft ELT 99-GY-001 | 0.38 | 0.72 |
| PreKote | Deft 02-Y-40A | Deft ELT 99-GY-001 | | | | 0.42 | 0.78 |
| Alodine 1600 | Crosslink | Deft ELT 99-GY-001 | PreKote | Crosslink | Deft ELT 99-GY-001 | 0.20 | 0.68 |
| PreKote | Crosslink | Deft ELT 99-GY-001 | | | | 0.18 | 0.69 |
| Alodine 1600 | Deft 02-Y-40A | Deft ELT 99-GY-001 | BAM-PPV | Deft 02-GN-084 | Deft ELT 99-GY-001 | 0.26 | 0.85 |
| BAM-PPV | Deft 02-Y-40A | Deft ELT 99-GY-001 | | | | 0.25 | 0.87 |
| Alodine 1600 | Deft 02-Y-40A | Deft ELT 99-GY-001 | PreKote | Deft 02-GN-084 | Deft ELT 99-GY-001 | 0.41 | 0.83 |
| PreKote | Deft 02-Y-40A | Deft ELT 99-GY-001 | | | | 0.40 | 0.81 |

**Table 32**: Reparability Results, Interface Adhesion Results

| Primary Coating System | | | Repair Coating System | | | Topcoat / Primer Interface | Primer / Pretreatment Interface |
|---|---|---|---|---|---|---|---|
| **Pretreatment** | **Primer** | **Topcoat** | **Pretreatment** | **Primer** | **Topcoat** | | |
| Alodine 1600 | Deft 02-Y-40A | Deft ELT 99-GY-001 | BAM-PPV | Deft 02-Y-40A | Deft ELT 99-GY-001 | 5A | 4A |
| BAM-PPV | Deft 02-Y-40A | Deft ELT 99-GY-001 | | | | 4A | 3A |
| Alodine 1600 | Crosslink | Deft ELT 99-GY-001 | BAM-PPV | Crosslink | Deft ELT 99-GY-001 | 5A | 3A |
| BAM-PPV | Crosslink | Deft ELT 99-GY-001 | | | | 5A | 3A |
| Alodine 1600 | Deft 02-Y-40A | Deft ELT 99-GY-001 | PreKote | Deft 02-Y-40A | Deft ELT 99-GY-001 | 5A | 4A |
| PreKote | Deft 02-Y-40A | Deft ELT 99-GY-001 | | | | 3A | 4A |
| Alodine 1600 | Crosslink | Deft ELT 99-GY-001 | PreKote | Crosslink | Deft ELT 99-GY-001 | 5A | 4A |
| PreKote | Crosslink | Deft ELT 99-GY-001 | | | | 4A | 5A |
| Alodine 1600 | Deft 02-Y-40A | Deft ELT 99-GY-001 | BAM-PPV | Deft 02-GN-084 | Deft ELT 99-GY-001 | 4A | 2A |
| BAM-PPV | Deft 02-Y-40A | Deft ELT 99-GY-001 | | | | 3A | 2A |
| Alodine 1600 | Deft 02-Y-40A | Deft ELT 99-GY-001 | PreKote | Deft 02-GN-084 | Deft ELT 99-GY-001 | 3A | 4A |
| PreKote | Deft 02-Y-40A | Deft ELT 99-GY-001 | | | | 3A | 3A |

**Table 33**: Reparability Results, Interface Pencil Hardness Results

| Primary Coating System | | | Repair Coating System | | | Topcoat / Primer Interface | Primer / Pretreatment Interface |
|---|---|---|---|---|---|---|---|
| **Pretreatment** | **Primer** | **Topcoat** | **Pretreatment** | **Primer** | **Topcoat** | | |
| Alodine 1600 | Deft 02-Y-40A | Deft ELT 99-GY-001 | BAM-PPV | Deft 02-Y-40A | Deft ELT 99-GY-001 | HB | HB |
| BAM-PPV | Deft 02-Y-40A | Deft ELT 99-GY-001 | | | | HB | HB |
| Alodine 1600 | Crosslink | Deft ELT 99-GY-001 | BAM-PPV | Crosslink | Deft ELT 99-GY-001 | 2H | F |
| BAM-PPV | Crosslink | Deft ELT 99-GY-001 | | | | 2H | F |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Alodine 1600 | Deft 02-Y-40A | Deft ELT 99-GY-001 | PreKote | Deft 02-Y-40A | Deft ELT 99-GY-001 | F | F |
| PreKote | Deft 02-Y-40A | Deft ELT 99-GY-001 | | | | F | F |
| Alodine 1600 | Crosslink | Deft ELT 99-GY-001 | PreKote | Crosslink | Deft ELT 99-GY-001 | F | F |
| PreKote | Crosslink | Deft ELT 99-GY-001 | | | | F | F |
| Alodine 1600 | Deft 02-Y-40A | Deft ELT 99-GY-001 | BAM-PPV | Deft 02-GN-084 | Deft ELT 99-GY-001 | F | F |
| BAM-PPV | Deft 02-Y-40A | Deft ELT 99-GY-001 | | | | F | F |
| Alodine 1600 | Deft 02-Y-40A | Deft ELT 99-GY-001 | PreKote | Deft 02-GN-084 | Deft ELT 99-GY-001 | F | F |
| PreKote | Deft 02-Y-40A | Deft ELT 99-GY-001 | | | | 5H | 5H |

**Table 34**: ASTM D 3359 and ASTM D 3363 Results for Topcoated Coatings Systems

| **Pretreatment** | **Primer** | **Topcoat** | **Initial ASTM D 3359 Method B (Adhesion)** | **Initial ASTM D 3363 (Hardness)** |
|---|---|---|---|---|
| Alodine 1600 | Deft 02-Y-40 | Deft 99-GY-001 | **4B** | F |
| | Deft 02-GN-084 | | **5B** | F |
| | Crosslink primer | | **5B** | F |
| Alodine 5200 | Deft 02-Y-40 | | **4B** | F |
| | Deft 02-GN-084 | | **5B** | F |
| | Crosslink primer | | **5B** | F |
| PreKote | Deft 02-Y-40 | | **4B** | F |
| | Deft 02-GN-084 | | **5B** | F |

| | | | | |
|---|---|---|---|---|
| | Crosslink primer | | **5B** | F |
| BAM-PPV | Deft 02-Y-40 | | **4B** | F |
| | Deft 02-GN-084 | | **2B** | F |
| | Crosslink primer | | **5B** | 2B |

The data from repair-ability suggested that the systems which were repaired with PreKote performed comparably to systems where PreKote was the original coating system material. The addition of the Crosslink primer did not alter coating performance. However, the use of BAM-PPV with the Crosslink primer as a repair system performed poorly as compared to systems with BAM-PPV and the Crosslink primer as the original coating system. These data suggest that the BAM-PPV and Crosslink primer system cannot be used as a repair coating, which significantly reduces the usefulness of this coating system for military applications. It is imperative that a coating system applied to a weapon system be repairable, otherwise the maintenance of that coating system becomes a burden on weapon system readiness requirements. The data showed that, as compared to chromated systems, non-chromated systems can provide comparable performance if the correct coating system stack-up is selected. An example of this performance was PreKote with MIL-PRF-23377 non-chromated primer and MIL-PRF-85285 Extended Life Topcoat (ELT). However, poor compatibility between the pretreatment and the primer or between the primer and the topcoat can cause failure of the coating system in several important tests, including but not limited to wet-tape adhesion, fluid immersion, pencil hardness, and salt spray resistance. An example of this performance was PreKote with experimental Crosslink primer and MIL-PRF-85285 ELT. A second example of this was BAM-PPV with experimental Crosslink primer and MIL-PRF-85285 ELT. In general, laboratory testing identified the weak areas for the experimental Crosslink primer when combined into a full military coating system.

#### 4.1.1.5 WPAFB Conclusions for Crosslink Primer Performance

The following conclusions have been determined by WPAFB following this two-year laboratory testing of the Crosslink primer system with various non-chromate pretreatments and topcoats. The results are in the form of bullets:

- Crosslink primer system passed the surface appearance, odor and drying time tests,
- BAM-PPV material is sensitive to molecular weight issues and that a change in the molecular weight of the polymer will cause a change in corrosion control performance,
- Crosslink corrosion-inhibiting primer performed best when it was combined with a CCC and topcoat,
- Reparability data also showed that BAM-PPV, Prekote with Crosslink primer system did not perform as well as the current non-chromate military coating,

- Crosslink did not perform well when it was combined with a non-chromated conversion coating (PreKote) or non-chromated pretreatment process (BAM-PPV,
- Uncertainty regarding the incompatibility between the BAM-PPV and the Crosslink corrosion-inhibiting primer which may be caused by the xylene-based solvent system in the Crosslink material, and Oxsol-100 solvent used for the BAM-PPV system,
- The data seems to suggests that the issues between these two materials was partly due to incompatible solvent packages,
- Finally the Crosslink primer system with CCC has been transitioned to the current ESTCP WP # 201132 Program for continued testing.

### 4.1.2 Laboratory Testing at ARL

Coupons AA 2024-T3 and 7075-T6 were pretreated, primed and topcoated at NAWCWD and NAWCAD. Pretreatments included Alodine 1200, Alodine 5700, Sur Tec 650, and BAM-PPV. Primers were MIL-PRF-23377C, MIL-PRF-23377N, MIL-PRF-53022, and Crosslink. The topcoat MIL-PRF-85285 was used over the Navy primers and Crosslink. MIL-DTL-64159 was applied over the MIL-PRF-53022 and Crosslink. This entire set was exposed to GM 9540 for up to 160 cycles. At every 20 cycles and upon completion of exposure, panels were rated using ASTM D 1654 method A for scribed regions and method B for unscribed regions. Final images were taken upon completion of exposure. Low carbon steel from KTA Tator were pretreated with D-D-P-15328 or Crosslink, and primed with MIL-DTL-53022 or Crosslink at ARL. Crosslink was mixed following instructions from the manufacturer and applied to the thicknesses cited in the wash primer or primer specifications. Panels were exposed to accelerated corrosion per ASTM B 117 and GM 9540. Salt fog panels were evaluated per ASTM D 1654 every 336 hours until failure while GM 9540 was evaluated every 20 cycles until failure or 160 cycles.

#### 4.1.2.1 Adhesion Studies on Crosslink Primer Systems

The adhesion values for the BAM-PPV were in line with previous testing. The adhesion of a coating on steel with BAM-PPV is half that of a similarly prepared panel with wash primer and one third that of an aluminum panel with TCP. The data showed that BAM-PPV with Crosslink is a better option than with MIL-PRF-53022. The lower adhesion values may be the reason behind the poorer blistering performance for the BAM-PPV treated panels. The standard pretreatments outperformed BAM-PPV in pull-off adhesion by more than a factor of two. Crosslink primer was slightly better than MIL-PRF-53022 for both substrate materials. Averaged values are presented in table 35.

**Table 35**: Averaged pull-off adhesion values

| Substrate | Adhesion (psi) |
|---|---|
| Steel/BAM-PPV/Crosslink | 611.96 |
| Steel/BAM-PPV/MIL-P-53022 | 552.64 |
| Steel/DoD-P-15328/MIL-P-53022 | 1367.67 |
| AA2024/BAM-PPV/Crosslink | 817.88 |
| AA2024/BAM-PPV/MIL-P-53022 | 629.63 |
| AA2024/TCP/Primer | 2784.13 |

#### 4.1.2.2 Accelerated Weathering Studies of Crosslink Primer Systems

AA 2024-T3 and AA 7075-T6 panels were pretreated, primed and topcoated at NAWCWD and NAWCAD. Pretreatments included Alodine 1200, Alodine 5700, Sur Tec 650 (TCP) and BAM-PPV. The primers that were used included MIL-PRF-23377C, MIL-PRF-23377N, MIL-PRF-53022, and Crosslink. The topcoat MIL-PRF-85285 was used over the Navy primers and Crosslink. MIL-DTL-64159 was applied over the MIL-PRF-53022 and Crosslink. This entire set was exposed to GM 9540 for up to 160 cycles. At every 20 cycles and upon completion of exposure, panels were rated using ASTM D 1654 method A for scribed regions and method B for unscribed regions. Final images were taken upon completion of exposure.

Low carbon steel from KTA Tator were pretreated with D-D-P-15328 or Crosslink, and primed with MIL-DTL-53022 or Crosslink at ARL. Crosslink was mixed following instructions from the manufacturer and applied to the thicknesses cited in the wash primer or primer specifications. Panels were exposed to accelerated corrosion per ASTM B 117 and GM 9540. NSS panels were evaluated per ASTM D 1654 every 336 hours until failure while GM 9540 was evaluated every 20 cycles until failure or 160 cycles.

##### 4.1.2.2.1 Neutral Salt Spray Testing of Crosslink Primer Systems

Steel panels from KTA Tator were coated using Crosslink as a primer, either direct to metal or with DoD-P-15328. These steel panels using the Crosslink primer in various coating systems were exposed to ASTM B 117 neutral salt spray exposure. The results showed that the Crosslink primer system when used as a pretreatment in conjunction with MIL-PRF-53022, provided equal to or slightly better performance as compared to the chromate containing DoD-P-15328 wash primer. This is especially true in the early part of the exposure. These results confirm comparable performance of the Crosslink primer system vs. the army wash primer (chromate based). The Crosslink continued to outperform wash primer for creep from scribe, however, blisters developed between 672 and 1008 hours across the entirety of the unscribed regions that led to their removal. The results are summarized in Table 36 with ratings and Figure 50 provides a representative image of the panels.

The following description provides the key to understanding the following tables regarding performance criteria in NSS chamber. BIF stands for blisters in field and

means that there was creep from scribe and blistering of the unscribed regions. The colors are a visual clue to performance and are as follows:

**Green** is ASTM D 1654 rating of 8-10
**Yellow** is ASTM D 1654 rating of 6-7
**Orange** is ASTM D 1654 rating of 4-5
**Red** is ASTM D 1654 rating of 1-3

A striped pattern is indicative of a rating containing BIF with the striped consisting of the colors associated with each half of the rating. If the ratings for BIF are the same, there will be a solid color field.

**Table 36**: ASTM D 1654 ratings of low carbon steel with Crosslink as a pretreatment and primer in ASTM B 117 salt fog exposure

| Pretreatment | Pretreatment | Panel ID | 336 Hour | 672 Hour | 1008 Hour | 1344 Hour | 1680 Hour | 2016 Hour |
|---|---|---|---|---|---|---|---|---|
| None | Crosslink | 1 | 8 BIF 0 | | | | | |
| None | Crosslink | 2 | 8 BIF 0 | | | | | |
| None | Crosslink | 3 | 8 BIF 0 | | | | | |
| None | Crosslink | 4 | 8 BIF 0 | | | | | |
| DoD-P-15328 | Crosslink | 1 | 8 BIF 0 | | | | | |
| DoD-P-15328 | Crosslink | 2 | 8 BIF 0 | | | | | |
| DoD-P-15328 | Crosslink | 3 | 8 BIF 0 | | | | | |
| DoD-P-15328 | Crosslink | 4 | 7 BIF 0 | | | | | |
| Crosslink | MIL-DTL-53022 | 1 | 7 | 4 | 4 BIF 0 | | | |
| Crosslink | MIL-DTL-53022 | 2 | 7 | 5 BIF 4 | 5 BIF 0 | | | |
| Crosslink | MIL-DTL-53022 | 3 | 7 | 5 BIF 5 | 5 BIF 0 | | | |
| Crosslink | MIL-DTL-53022 | 4 | 7 | 5 BIF 5 | 5 BIF 0 | | | |
| DoD-P-15328 | MIL-DTL-53022 | 1 | 6 | 2 BIF 6 | 2 BIF 4 | 2 BIF 4 | 2 BIF 4 | 2 BIF 3 |
| DoD-P-15328 | MIL-DTL-53022 | 2 | 6 | 3 BIF 6 | 2 BIF 5 | 2 BIF 5 | 2 BIF 3 | 2 BIF 3 |
| DoD-P-15328 | MIL-DTL-53022 | 3 | 6 | 3 BIF 7 | 3 BIF 4 | 3 BIF 2 | 3 BIF 1 | 3 BIF 0 |
| DoD-P-15328 | MIL-DTL-53022 | 4 | 7 | 4 BIF 7 | 4 BIF 5 | 4 BIF 3 | 4 BIF 3 | 4 BIF 2 |

**Figure 50**: Crosslink direct to metal, DoD-P-15328 with Crosslink primer, Crosslink as pretreatment with MIL-PRF-53022, and DoD-P-15328 with MIL-PRF-53022 following NSS exposure

#### 4.1.2.2.2 GM9540P Accelerated Corrosion Test

The Alodine 1200 pretreated AA 2024-T3 all performed well in GM9540 accelerated exposure. As can be seen in table 37, the Cr(VI) primer, MIL-PRF-23377C clearly had little damage after the exposure. The Crosslink primer had similar creep back from scribe performance but had several blisters appear on each panel in the unscribed regions. The chromate-free version of MIL-PRF-23377N had the poorest corrosion resistance from an intentional flaw. Figure 51 shows a representative image of each pretreatment following exposure.

**Table 37**: ASTM D 1654 ratings for AA 2024-T3 with Alodine 1200 pretreatment and MIL-PRF-85285 topcoat

| Substrate | Pretreatment | Primer | Topcoat | 20 Cycle | 40 Cycle | 60 Cycle | 80 Cycle | 100 Cycle | 120 Cycle | 140 Cycle | 160 Cycle |
|---|---|---|---|---|---|---|---|---|---|---|---|
| AL 2024 | Alodine 1200 | 23377C | 85285 | 10 | 10 | 9 | 9 | 9 | 9 | 8 | 8 |
| AL 2024 | Alodine 1200 | 23377C | 85285 | 10 | 10 | 9 | 9 | 9 | 9 | 9 | 8 |
| AL 2024 | Alodine 1200 | 23377C | 85285 | 10 | 10 | 9 | 9 | 9 | 9 | 8 | 8 |
| AL 2024 | Alodine 1200 | 23377C | 85285 | 10 | 9 | 9 | 9 | 9 | 9 | 9 | 9 |
| AL 2024 | Alodine 1200 | 23377C | 85285 | 10 | 10 | 9 | 9 | 9 | 8 | 8 | 8 |
| AL 2024 | Alodine 1200 | 23377N | 85285 | 9 | 9 | 8 | 7 | 7 | 6 | 6 | 6 |
| AL 2024 | Alodine 1200 | 23377N | 85285 | 9 | 9 | 8 | 7 | 7 | 7 | 7 | 6 |
| AL 2024 | Alodine 1200 | 23377N | 85285 | 9 | 9 | 8 | 7 | 7 | 7 | 6 | 6 |
| AL 2024 | Alodine 1200 | 23377N | 85285 | 9 | 9 | 7 | 6 | 6 | 5 | 5 | 5 |
| AL 2024 | Alodine 1200 | 23377N | 85285 | 9 | 8 | 7 | 7 | 7 | 7 | 6 | 5 |
| AL 2024 | Alodine 1200 | Crosslink | 85285 | 10 | 9 BIF 8 | 9 BIF 7 | 9 BIF 7 | 8 BIF 7 | 8 BIF 7 | 8 BIF 7 | 8 BIF 7 |
| AL 2024 | Alodine 1200 | Crosslink | 85285 | 10 | 9 | 9 | 9 | 9 | 9 | 9 | 8 |
| AL 2024 | Alodine 1200 | Crosslink | 85285 | 10 | 9 | 9 BIF 9 | 9 BIF 9 | 9 BIF 8 | 9 BIF 8 | 9 BIF 8 | 7 BIF 7 |
| AL 2024 | Alodine 1200 | Crosslink | 85285 | 10 | 9 | 9 BIF 8 | 9 BIF 8 | 9 BIF 7 | 9 BIF 7 | 8 BIF 7 | 8 BIF 7 |
| AL 2024 | Alodine 1200 | Crosslink | 85285 | 9 BIF 8 | 9 BIF 7 | 9 BIF 7 | 9 BIF 7 | 9 BIF 7 | 9 BIF 7 | 9 BIF 7 | 9 BIF 7 |

**Figure 51**: AA 2024-T3 panels Pretreated with Alodine 1200 and topcoated with MIL-PRF-85285. Primers are MIL-PRF-23377C, MIL-PRF-23377N, and Crosslink following 120 cycles GM 9540 exposure

When the pretreatment was changed to Sur Tec 650 (TCP), the performance of the chromated primer was unaffected. The combination of Sur Tec 650 and the non-chrome primer had corrosion resistance that approached that of the chromated version. The combination with Crosslink had a slight degradation of corrosion resistance at the scribe and an increased presence of blisters away from the scribe. Table 38 and figure 52 show the ratings and representative images of these panels.

**Table 38**: ASTM D 1654 ratings for AA 2024 with Sur Tec 650 pretreatment and MIL-PRF- 85285 topcoat

| Substrate | Pretreatment | Primer | Topcoat | 20 Cycle | 40 Cycle | 60 Cycle | 80 Cycle | 100 Cycle | 120 Cycle | 140 Cycle | 160 Cycle |
|---|---|---|---|---|---|---|---|---|---|---|---|
| AL 2024 | Sur Tec 650 | 23377C | 85285 | 10 | 10 | 10 | 10 | 10 | 10 | 9 | 9 |
| AL 2024 | Sur Tec 650 | 23377C | 85285 | 10 | 10 | 10 | 10 | 9 | 9 | 9 | 9 |
| AL 2024 | Sur Tec 650 | 23377C | 85285 | 10 | 9 | 9 | 9 | 9 | 9 | 9 | 8 |
| AL 2024 | Sur Tec 650 | 23377C | 85285 | 10 | 9 | 9 | 9 | 9 | 9 | 9 | 9 |
| AL 2024 | Sur Tec 650 | 23377C | 85285 | 10 | 10 | 10 | 9 | 9 | 9 | 9 | 9 |
| AL 2024 | Sur Tec 650 | 23377N | 85285 | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 |
| AL 2024 | Sur Tec 650 | 23377N | 85285 | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 |
| AL 2024 | Sur Tec 650 | 23377N | 85285 | 9 | 9 | 9 | 9 | 8 | 8 | 8 | 8 |
| AL 2024 | Sur Tec 650 | 23377N | 85285 | 9 | 9 | 9 | 8 | 8 | 8 | 8 | 8 |
| AL 2024 | Sur Tec 650 | 23377N | 85285 | 9 | 9 | 8 | 8 | 8 | 7 | 7 | 7 |
| AL 2024 | Sur Tec 650 | Crosslink | 85285 | 9 BIF 7 | 9 BIF 7 | 9 BIF 6 | 9 BIF 6 | 9 BIF 6 | 9 BIF 6 | 9 BIF 6 | 9 BIF 6 |
| AL 2024 | Sur Tec 650 | Crosslink | 85285 | 9 BIF 8 | 9 BIF 8 | 9 BIF 7 | 9 BIF 7 | 9 BIF 7 | 9 BIF 7 | 8 BIF 7 | 8 BIF 7 |
| AL 2024 | Sur Tec 650 | Crosslink | 85285 | 9 BIF 6 | 9 BIF 6 | 9 BIF 5 | 9 BIF 5 | 9 BIF 5 | 9 BIF 5 | 9 BIF 5 | 9 BIF 5 |
| AL 2024 | Sur Tec 650 | Crosslink | 85285 | 9 BIF 7 | 9 BIF 7 | 8 BIF 7 | 7 BIF 7 | 7 BIF 7 | 6 BIF 7 | 6 BIF 7 | 6 BIF 7 |
| AL 2024 | Sur Tec 650 | Crosslink | 85285 | 9 BIF 8 | 9 BIF 8 | 8 BIF 8 | 8 BIF 8 | 8 BIF 8 | 7 BIF 8 | 6 BIF 8 | 6 BIF 8 |

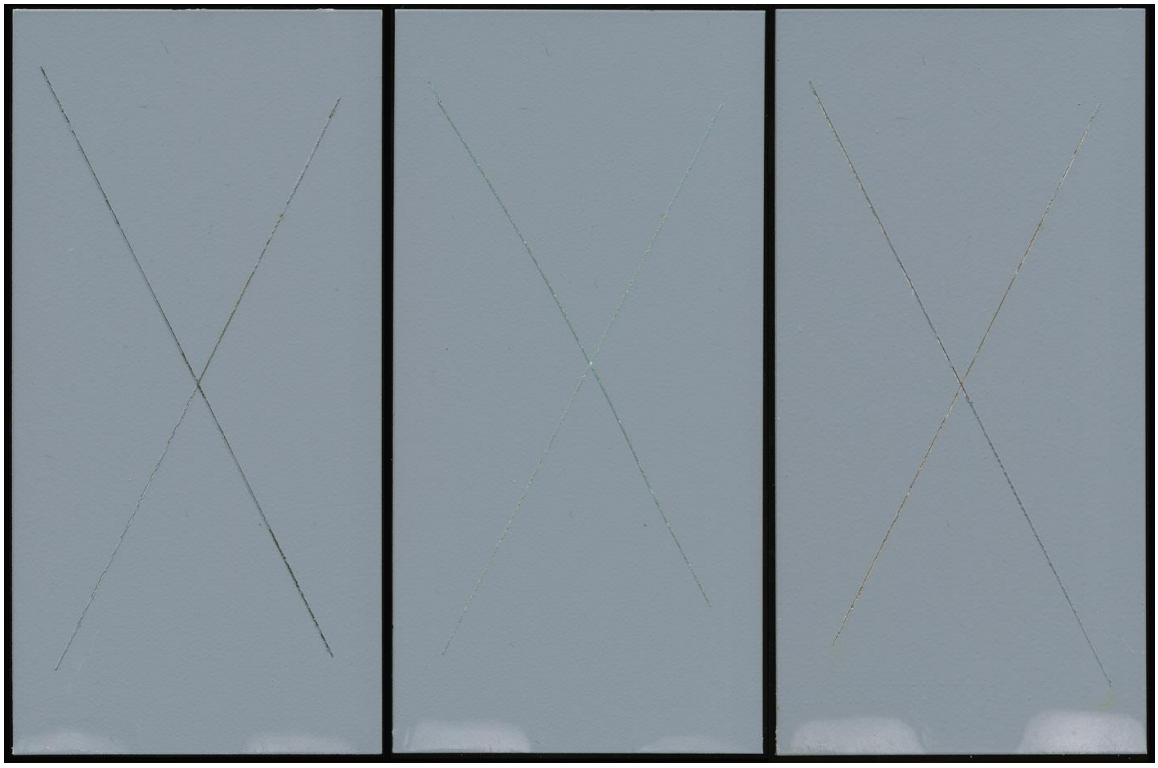


**Figure 52**: AA 2024-T3 panels Pretreated with Sur Tec 650 and topcoated with MIL-PRF-85285. Primers are MIL-PRF-23377C, MIL-PRF-23377N, and Crosslink following 120 cycles GM 9540 exposure

When BAM-PPV is used as the pretreatment for AA 2024-T3, there is a significant drop off in corrosion resistance for the non-chrome alternatives. The MIL-PRF-23377C had only minor corrosion damage and no blistering in the unscribed regions. The non-chrome MIL-PRF-23377N primer provided borderline protection for 40 cycles but was unacceptable after 120 cycles. The Crosslink primer developed small blisters across the entire surface within 20 cycles. There was also debonding at the scribe that would have been an issue had the blistering failure not occurred. ASTM D 1654 ratings are in table 39 with representative images of each set contained in figure 53.

Table 40 shows the ratings of MIL-PRF-53022 and Crosslink over BAM-PPV and Alodine 5700 treated AA 2024 with MIL-DTL-64159 as the topcoat. The MIL-PRF 53022 performed similarly to the MIL-PRF-23377N in that borderline protection was provided through 40 cycles GM 9540 but that protection fell off sharply after 120 cycles and was unacceptable at 160 cycles. Again, when the Crosslink primer was used instead of the military primer, the entire coating developed many small blisters. However, there appeared to be better adhesion at the scribe. When Alodine 5700 is substituted for BAM-PPV for the above primer/topcoat combinations, the performance in GM 9540 improves. The system with MIL-PRF 53022 provides marginal protection all the way to 160 cycles. The Crosslink primed system provides even better creep from scribe resistance throughout the exposure. However, this combination over Alodine 5700 continues to

have a slight blistering problem, though not to the extent that it did over BAM-PPV. Representative images taken at the end of exposure are presented in Figure 54.

**Table 39**: ASTM D 1654 ratings for AA 2024-T3 with Sur Tec 650 pretreatment and MIL-PRF- 85285 topcoat

| Substrate | Pretreatment | Primer | Topcoat | 20 Cycle | 40 Cycle | 60 Cycle | 80 Cycle | 100 Cycle | 120 Cycle |
|---|---|---|---|---|---|---|---|---|---|
| AL 2024 | BAM-PPV | 23377C | 85285 | 10 | 10 | 8 | 8 | 8 | 8 |
| AL 2024 | BAM-PPV | 23377C | 85285 | 10 | 10 | 10 | 10 | 10 | 9 |
| AL 2024 | BAM-PPV | 23377C | 85285 | 10 | 9 | 9 | 9 | 8 | 8 |
| AL 2024 | BAM-PPV | 23377C | 85285 | 10 | 10 | 9 | 9 | 9 | 9 |
| AL 2024 | BAM-PPV | 23377C | 85285 | 10 | 10 | 9 | 8 | 8 | 8 |
| AL 2024 | BAM-PPV | 23377N | 85285 | 8 | 8 | 7 | 5 | 5 | 5 |
| AL 2024 | BAM-PPV | 23377N | 85285 | 8 BIF 9 | 7 BIF 9 | 6 BIF 9 | 5 | 5 | 5 |
| AL 2024 | BAM-PPV | 23377N | 85285 | 8 | 7 | 6 | 5 | 5 | 5 |
| AL 2024 | BAM-PPV | 23377N | 85285 | 7 | 6 | 6 | 6 | 5 | 5 |
| AL 2024 | BAM-PPV | 23377N | 85285 | 8 | 7 | 6 | 5 | 5 | 4 |
| AL 2024 | BAM-PPV | Crosslink | 85285 | 7 BIF 0 | | | | | |
| AL 2024 | BAM-PPV | Crosslink | 85285 | 7 BIF 0 | | | | | |
| AL 2024 | BAM-PPV | Crosslink | 85285 | 7 BIF 0 | | | | | |
| AL 2024 | BAM-PPV | Crosslink | 85285 | 7 BIF 0 | | | | | |
| AL 2024 | BAM-PPV | Crosslink | 85285 | 7 BIF 0 | | | | | |

**Figure 53**: AA 2024-T3 panels pretreated with BAM-PPV and topcoated with MIL-PRF-85285. Primers are MIL-PRF-23377C @120 cycles, MIL-PRF-23377N, @120 cycles and Crosslink @20 cycles

**Table 40**: ASTM D 1654 ratings for Al 2024 with BAM-PPV and Alodine 1200 pretreatments, MIL-PRF-53022 and Crosslink primers and MIL-DTL-64159 topcoat

| Substrate | Pretreatment | Primer | Topcoat | 20 Cycle | 40 Cycle | 60 Cycle | 80 Cycle | 100 Cycle | 120 Cycle | 140 Cycle | 160 Cycle |
|---|---|---|---|---|---|---|---|---|---|---|---|
| AL 2024 | BAM-PPV | 53022 | 64159 | 8 | 6 | 5 | 5 | 5 | 4 | 3 | 2 |
| AL 2024 | BAM-PPV | 53022 | 64159 | 8 | 7 | 7 | 6 | 5 | 5 | 3 | 3 |
| AL 2024 | BAM-PPV | 53022 | 64159 | 8 | 7 | 6 | 5 | 5 | 5 | 5 | 5 |
| AL 2024 | BAM-PPV | 53022 | 64159 | 8 | 7 | 6 | 5 | 5 | 5 | 4 | 4 |
| AL 2024 | BAM-PPV | 53022 | 64159 | 8 | 7 | 6 | 5 | 4 | 4 | 4 | 3 |
| AL 2024 | BAM-PPV | Crosslink | 64159 | 9 BIF 0 | | | | | | | |
| AL 2024 | BAM-PPV | Crosslink | 64159 | 9 BIF 0 | | | | | | | |
| AL 2024 | BAM-PPV | Crosslink | 64159 | 9 BIF 0 | | | | | | | |
| AL 2024 | BAM-PPV | Crosslink | 64159 | 9 BIF 0 | | | | | | | |
| AL 2024 | BAM-PPV | Crosslink | 64159 | 8 BIF 0 | | | | | | | |
| AL 2024 | Alodine 5700 | 53022 | 64159 | 8 | 7 | 7 | 6 | 6 | 6 | 6 | 6 |
| AL 2024 | Alodine 5700 | 53022 | 64159 | 8 | 7 | 7 | 7 | 6 | 6 | 6 | 6 |
| AL 2024 | Alodine 5700 | 53022 | 64159 | 8 | 7 | 7 | 6 | 6 | 6 | 6 | 6 |
| AL 2024 | Alodine 5700 | 53022 | 64159 | 8 | 7 | 7 | 7 | 7 | 6 | 6 | 6 |
| AL 2024 | Alodine 5700 | 53022 | 64159 | 8 | 7 | 7 | 7 | 6 | 6 | 6 | 6 |
| AL 2024 | Alodine 5700 | Crosslink | 64159 | 9 BIF 7 | 9 BIF 7 | 9 BIF 6 | 9 BIF 6 | 9 BIF 6 | 9 BIF 6 | 8 BIF 6 | 6 BIF 6 |
| AL 2024 | Alodine 5700 | Crosslink | 64159 | 9 BIF 5 | 9 BIF 5 | 9 BIF 5 | 9 BIF 5 | 9 BIF 5 | 9 BIF 5 | 8 BIF 5 | 7 BIF 5 |
| AL 2024 | Alodine 5700 | Crosslink | 64159 | 9 | 9 BIF 9 | 9 BIF 6 | 9 BIF 6 | 7 BIF 6 | 7 BIF 6 | 7 BIF 6 | 7 BIF 6 |
| AL 2024 | Alodine 5700 | Crosslink | 64159 | 9 BIF 8 | 9 BIF 8 | 9 BIF 7 | 9 BIF 7 | 9 BIF 7 | 9 BIF 7 | 7 BIF 7 | 7 BIF 7 |
| AL 2024 | Alodine 5700 | Crosslink | 64159 | 9 BIF 7 | 9 BIF 7 | 9 BIF 7 | 9 BIF 7 | 9 BIF 7 | 9 BIF 7 | 8 BIF 7 | 7 BIF 7 |

**Figure 54**: AA 2024-T3 panels with BAM-PPV/MIL-PRF-53022, BAM-PPV/Crosslink primer, Alodine 5700/MIL-PRF-53022, and Alodine 5700/Crosslink primer. All are topcoated with MIL-DTL-64159. Images are following 120 cycles GM 9540 except BAM-PPV/Crosslink which was taken following 20 cycles

As can be seen in Table 41 and Figure 55, the combination of Alodine 1200 as pretreatment over AA 7075-T6 performed well with any primer/topcoat combinations. There was no blistering anywhere on the panel including the areas immediately adjacent to the scribe through the coatings. There was only minor discoloration of this scribe mark after 160 cycles of GM 9540.

Substituting Sur Tec 650 for Alodine 1200 for the above combinations had no impact on the MIL-PRF-23377C and MIL-PRF-23377N performances. As can be seen in table 42, the creep from scribe performance of the Crosslink system over AA 7075-T6 degraded slightly. However, there was an appreciable and unacceptable loss of blistering resistance in the unscribed areas of these panels (see Figure 56).

**Table 41**: ASTM D 1654 ratings of AA 7075-T6 with Alodine1200 pretreatment and MIL-PRF-85285 topcoat

| Substrate | Pretreatment | Primer | Topcoat | 20 Cycle | 40 Cycle | 60 Cycle | 80 Cycle | 100 Cycle | 120 Cycle | 140 Cycle | 160 Cycle |
|---|---|---|---|---|---|---|---|---|---|---|---|
| AL 7075 | Alodine 1200S | 23377C | 85285 | 10 | 10 | 10 | 10 | 9 | 9 | 9 | 9 |
| AL 7075 | Alodine 1200S | 23377C | 85285 | 10 | 10 | 10 | 10 | 10 | 9 | 9 | 9 |
| AL 7075 | Alodine 1200S | 23377C | 85285 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 8 |
| AL 7075 | Alodine 1200S | 23377C | 85285 | 10 | 8 | 8 | 8 | 8 | 8 | 8 | 8 |
| AL 7075 | Alodine 1200S | 23377C | 85285 | 10 | 9 | 9 | 9 | 9 | 8 | 8 | 8 |
| AL 7075 | Alodine 1200S | 23377N | 85285 | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 |
| AL 7075 | Alodine 1200S | 23377N | 85285 | 9 | 9 | 9 | 9 | 8 | 8 | 8 | 8 |
| AL 7075 | Alodine 1200S | 23377N | 85285 | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 |
| AL 7075 | Alodine 1200S | 23377N | 85285 | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 |
| AL 7075 | Alodine 1200S | 23377N | 85285 | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 |
| AL 7075 | Alodine 1200S | Crosslink | 85285 | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 |
| AL 7075 | Alodine 1200S | Crosslink | 85285 | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 |
| AL 7075 | Alodine 1200S | Crosslink | 85285 | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 |
| AL 7075 | Alodine 1200S | Crosslink | 85285 | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 |
| AL 7075 | Alodine 1200S | Crosslink | 85285 | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 |

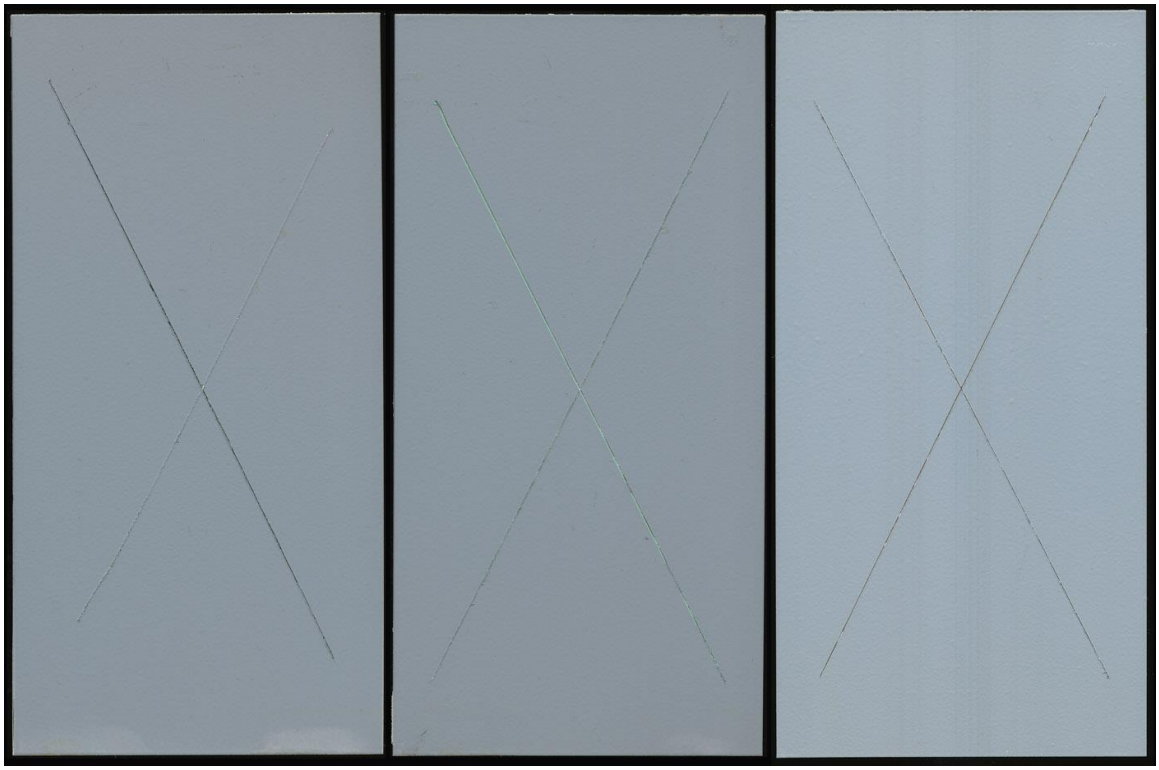


**Figure 55**: AA 2024-T3 panels Pretreated with Alodine 1200 and topcoated with MIL-PRF-85285. Primers are MIL-PRF-23377C, MIL-PRF-23377N, and Crosslink following 120 cycles GM 9540 exposure

**Table 42**: ASTM D 1654 ratings for AA 7075-T6 with Sur Tec 650 pretreatment and MIL-PRF- 85285 topcoat

| Substrate | Pretreatment | Primer | Topcoat | 20 Cycle | 40 Cycle | 60 Cycle | 80 Cycle | 100 Cycle | 120 Cycle | 140 Cycle | 160 Cycle |
|---|---|---|---|---|---|---|---|---|---|---|---|
| AL 2024 | Sur Tec 650 | 23377C | 85285 | 10 | 10 | 10 | 10 | 10 | 10 | 9 | 9 |
| AL 2024 | Sur Tec 650 | 23377C | 85285 | 10 | 10 | 10 | 10 | 9 | 9 | 9 | 9 |
| AL 2024 | Sur Tec 650 | 23377C | 85285 | 10 | 9 | 9 | 9 | 9 | 9 | 9 | 8 |
| AL 2024 | Sur Tec 650 | 23377C | 85285 | 10 | 9 | 9 | 9 | 9 | 9 | 9 | 9 |
| AL 2024 | Sur Tec 650 | 23377C | 85285 | 10 | 10 | 10 | 9 | 9 | 9 | 9 | 9 |
| AL 2024 | Sur Tec 650 | 23377N | 85285 | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 |
| AL 2024 | Sur Tec 650 | 23377N | 85285 | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 |
| AL 2024 | Sur Tec 650 | 23377N | 85285 | 9 | 9 | 9 | 9 | 8 | 8 | 8 | 8 |
| AL 2024 | Sur Tec 650 | 23377N | 85285 | 9 | 9 | 9 | 8 | 8 | 8 | 8 | 8 |
| AL 2024 | Sur Tec 650 | 23377N | 85285 | 9 | 9 | 8 | 8 | 8 | 7 | 7 | 7 |
| AL 2024 | Sur Tec 650 | Crosslink | 85285 | 9 BIF 7 | 9 BIF 7 | 9 BIF 6 | 9 BIF 6 | 9 BIF 6 | 9 BIF 6 | 9 BIF 6 | 9 BIF 6 |
| AL 2024 | Sur Tec 650 | Crosslink | 85285 | 9 BIF 8 | 9 BIF 8 | 9 BIF 7 | 9 BIF 7 | 9 BIF 7 | 9 BIF 7 | 8 BIF 7 | 8 BIF 7 |
| AL 2024 | Sur Tec 650 | Crosslink | 85285 | 9 BIF 6 | 9 BIF 6 | 9 BIF 5 | 9 BIF 5 | 9 BIF 5 | 9 BIF 5 | 9 BIF 5 | 9 BIF 5 |
| AL 2024 | Sur Tec 650 | Crosslink | 85285 | 9 BIF 7 | 9 BIF 7 | 8 BIF 7 | 7 BIF 7 | 7 BIF 7 | 6 BIF 7 | 6 BIF 7 | 6 BIF 7 |
| AL 2024 | Sur Tec 650 | Crosslink | 85285 | 9 BIF 8 | 9 BIF 8 | 8 BIF 8 | 8 BIF 8 | 8 BIF 8 | 7 BIF 8 | 6 BIF 8 | 6 BIF 8 |

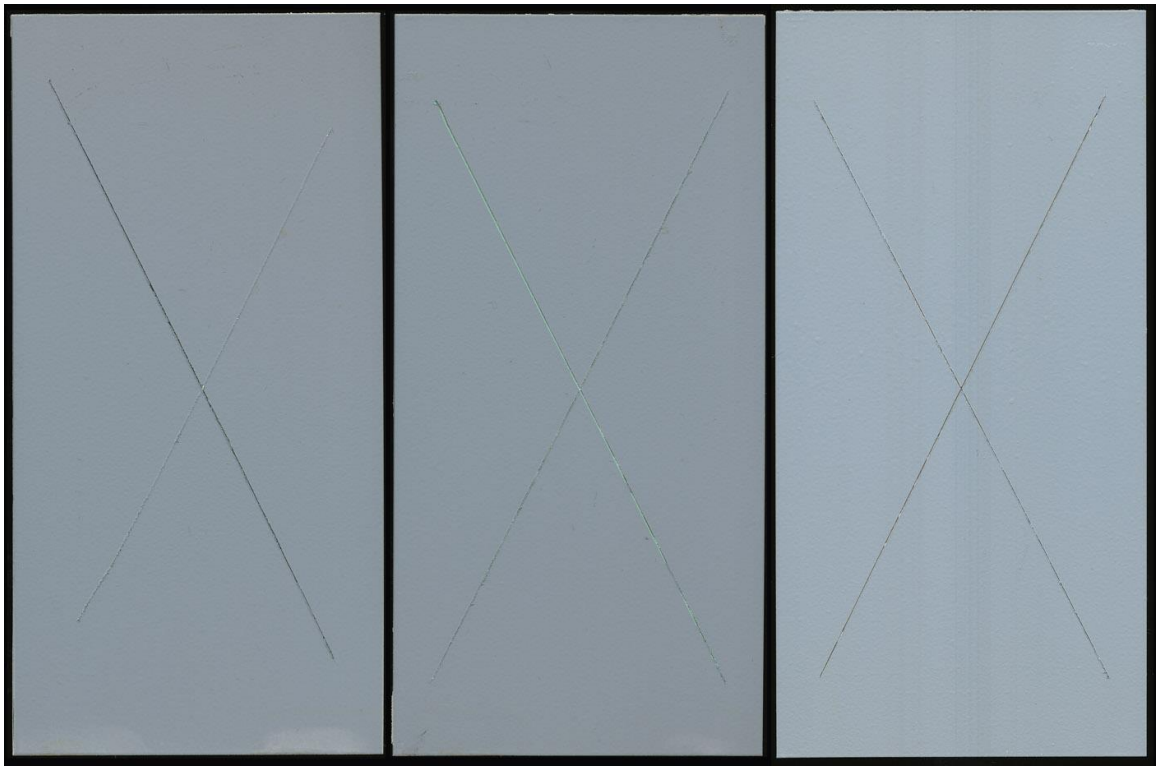


**Figure 56**: AA 7075-T6 panels pretreated with Sur Tec 650 and topcoated with MIL-PRF-85285. Primers are MIL-PRF-23377C, MIL-PRF-23377N, and Crosslink following 120 cycles GM 9540 exposure

Steel panels from KTA Tator using Crosslink as a primer, either direct to metal or with DoD-P-15328 did not provide adequate blister resistance for the unscribed regions in 20 to 40 cycles of GM 9540. These panels were not exposed long enough to adequately characterize the creep from scribe performance. As can be seen in Table 43 when Crosslink was used as a pretreatment in conjunction with MIL-PRF-53022, the performance of the Crosslink is equal to or slightly better than the chromate containing DoD-P-15328. This is especially true in the early part of the exposure (see Figure 57).

**Table 43**: ASTM D 1654 ratings of low carbon steel with Crosslink as a pretreatment and primer in GM 9540 cyclic exposure

| Pretreatment | Primer | Panel ID | 20 Cycle | 40 Cycle | 60 Cycle | 80 Cycle | 100 Cycle | 120 Cycle | 140 Cycle | 160 Cycle |
|---|---|---|---|---|---|---|---|---|---|---|
| None | Crosslink | 1 | 8 BIF 0 | | | | | | | |
| None | Crosslink | 2 | 7 BIF 0 | | | | | | | |
| None | Crosslink | 3 | 8 BIF 0 | | | | | | | |
| None | Crosslink | 4 | 8 BIF 0 | | | | | | | |
| DoD-P-15328 | Crosslink | 1 | 8 BIF 7 | 7 BIF 0 | | | | | | |
| DoD-P-15328 | Crosslink | 2 | 8 BIF 5 | 7 BIF 0 | | | | | | |
| DoD-P-15328 | Crosslink | 3 | 8 BIF 5 | 7 BIF 0 | | | | | | |
| DoD-P-15328 | Crosslink | 4 | 8 BIF 4 | 7 BIF 0 | | | | | | |
| Crosslink | MIL-DTL-53022 | 1 | 6 | 5 | 5 | 5 | 4 | 4 | 3 | 3 |
| Crosslink | MIL-DTL-53022 | 2 | 7 | 6 | 6 | 5 | 4 | 4 | 4 | 4 |
| Crosslink | MIL-DTL-53022 | 3 | 6 BIF 7 | 6 BIF 7 | 5 BIF 7 | 5 BIF 7 | 4 BIF 7 | 4 BIF 6 | 4 BIF 5 | 4 BIF 5 |
| Crosslink | MIL-DTL-53022 | 4 | 7 | 7 | 7 | 5 | 5 | 5 | 5 | 5 |
| DoD-P-15328 | MIL-DTL-53022 | 1 | 7 | 6 | 6 | 5 | 5 | 5 | 5 | 4 |
| DoD-P-15328 | MIL-DTL-53022 | 2 | 6 | 5 | 4 | 4 | 4 | 3 | 3 | 3 |
| DoD-P-15328 | MIL-DTL-53022 | 3 | 6 | 5 BIF 9 | 5 BIF 7 | 4 BIF 6 | 3 BIF 6 | 3 BIF 6 | 2 BIF 6 | 2 BIF 6 |
| DoD-P-15328 | MIL-DTL-53022 | 4 | 6 BIF 8 | 5 BIF 7 | 5 BIF 7 | 4 BIF 6 | 4 BIF 6 | 3 BIF 6 | 2 BIF 6 | 2 BIF 6 |

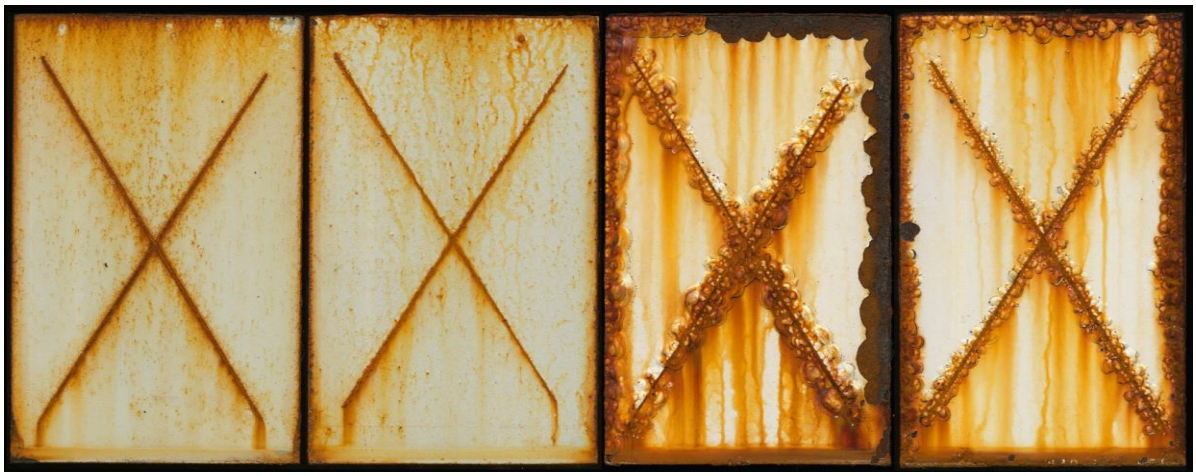


**Figure 57**: Crosslink direct to metal, DoD-P-15328 with Crosslink primer, Crosslink as pretreatment with MIL-PRF-53022, and DoD-P-15328 with MIL-PRF-53022 following 20 cycles GM 9540 exposure

#### 4.1.2.3 ARL Conclusions for Crosslink Primer Performance

The following conclusions can be obtained from the two-year laboratory testing of the Crosslink primer systems. The conclusions are summarized as bullets.

- The adhesion values for the BAM-PPV were in line with previous testing done under ESTCP Project # WP 200527.
- The adhesion of a coating on steel with BAM-PPV is half that of a similarly prepared panel with wash primer and one third that of an aluminum panel with TCP.
- The data indicate that BAM-PPV with Crosslink is a better option than with MIL-PRF-53022.
- The lower adhesion values may be the reason behind the poorer blistering performance for the BAM-PPV treated panels.
- Crosslink primer had blistering issues with every substrate/ pretreatment combination that it encountered except AA 7075-T6 with Alodine 1200 as pretreatment. Despite the blistering, the Crosslink primer had good creep from scribe performance when compared to the Army primer and topcoat over AA 2024-T3/Alodine 5700.
- When Crosslink was used as the pretreatment on steel as a substitute for the DoD-P-15328 wash primer pretreatment, the Crosslink performed better in GM 9540 than did the Cr(VI) wash primer pretreatment.
- The Crosslink as a direct to metal coating and as a substitute for MIL-PRF-53022 was susceptible to blistering in both accelerated exposures and did not last past the first rating period.
- When low carbon steel is the substrate, Crosslink showed promise as a substitute for the DoD-P-15328, Cr(VI) wash primer. The Crosslink primer had similar creep from scribe performance as the wash primer. Blistering manifested itself in ASTM B 117 after 672 hours. Blistering was not a problem in GM 9540. Crosslink could provide the Army's CARC system with a field applied option that is chrome-free.

### 4.1.3 Laboratory Testing at NAWCAD/NAWCWD

NAWCAD in cooperation with NAWCWD tested several Crosslink primer systems for adhesion, accelerated weathering tests and fluid resistance testing. The alternative pretreatment coating BAM-PPV was provided to NAWCAD. BAM-PPV was coated onto metal substrates via HVLP spray using ~1 wt% solution of BAM-PPV powder dissolved in Oxsol-100 solvent. After dissolution of the polymer into the solvent the BAM-PPV was sprayed onto the test panels. The test panel substrates were 3" x 6" AA 2024-T3 and AA 7075-T6. All Cr(VI) and TCP panels were pretreated at NAWCAD as follows:

- Cleaned using Turco 4215 mildly alkaline cleaner for 15 minutes at 120°F.
- Deoxidized using Turco Smut-Go deoxidizer and desmutter at 69°F for 2 minutes.
- Pretreated in accordance with the Alodine 1200S and SurTec 650 ChromitAL-(TCP) recommended parameters.

All test panels were finished with either Crosslink primer, or one coat of a VOC compliant epoxy-polyamide primer conforming to either MIL-PRF-23377 Class C or Class N to a dry film thickness of 0.0006 to 0.0009 inch (0.6 to 0.9 mil). All test panels received a topcoat conforming to MIL-PRF-85285. After paint application, test panels were allowed to cure in accordance with primer specification prior to testing.

#### 4.1.3.1 Adhesion Testing for Crosslink Primer Systems

Dry tape (crosshatch) adhesion testing was performed on the Crosslink primer systems to determine the adhesion between the substrate, pretreatment, primer, and topcoat interfaces. This test was performed in accordance with ASTM D 3359, Method B. The description of the rating scale, as taken from ASTM D 3359, is given in Section 3.1.1.2.

##### 4.1.3.1.1 Crosshatch Adhesion Testing of Crosslink Primer Systems

The Crosslink coatings must demonstrate an adhesion rating of 4B or 5B which are then given a "pass" rating. The test panel data are provided in the graph form in Figure 58. The majority of Crosslink coated test panels did not demonstrate acceptable adhesion behavior and the dry tape adhesion test panels are shown in Figures 59-77 with all panels identified by the metal substrate used during the test.

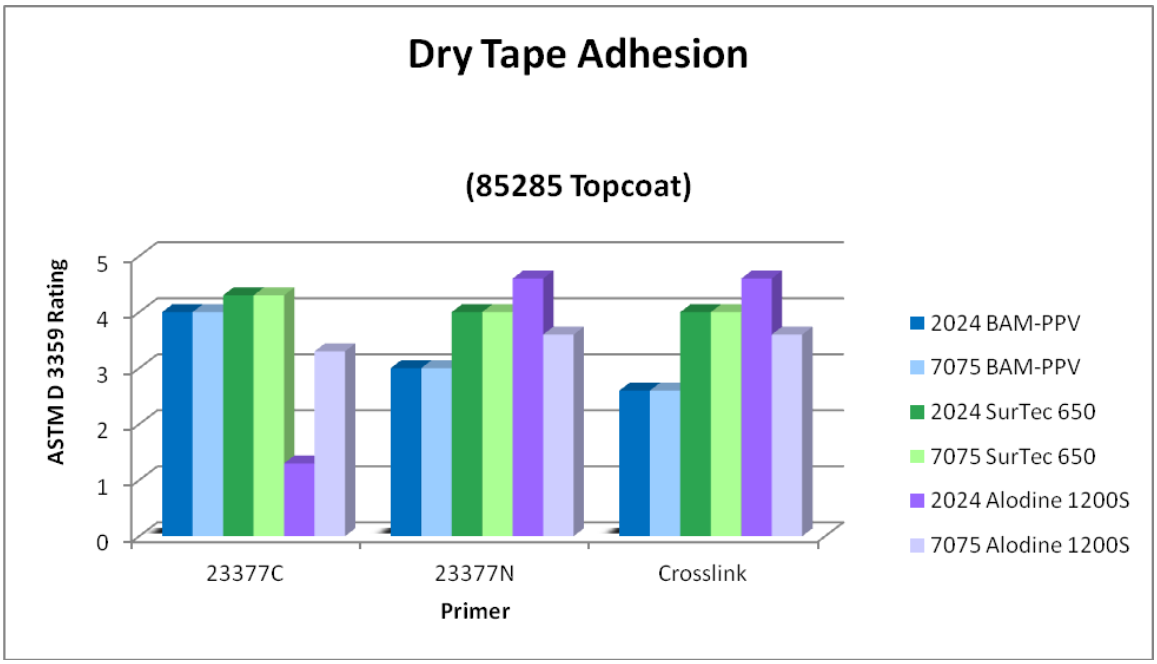



**Figure 58**: Dry Adhesion Results per ASTM D 3359, Method B

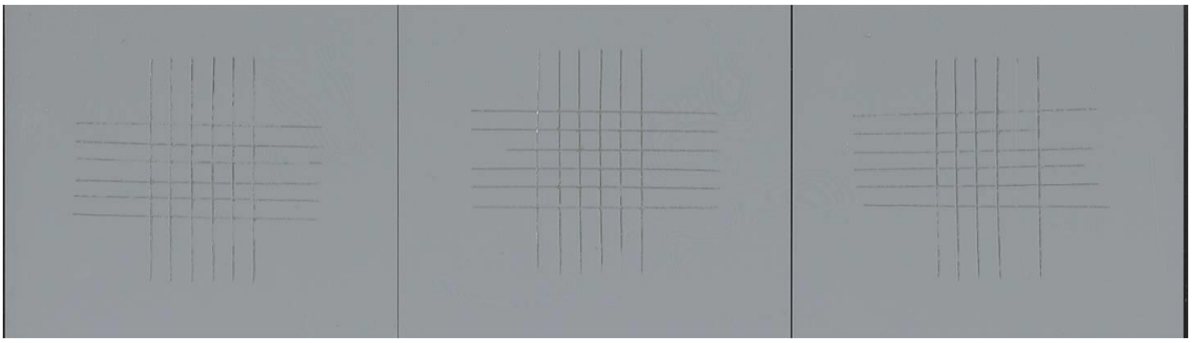


**Figure 59**: AA2024-T3 – SurTec 650 + 23377C + 85285 (ASTM D3359, Method B)

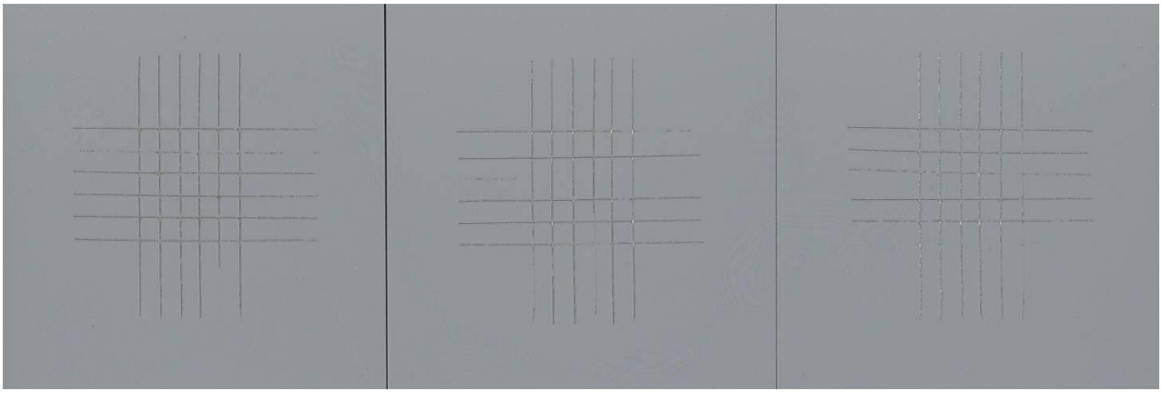


**Figure 60**: AA7075-T6 SurTec 650 + 23377C + 85285 (ASTM D3359, Method B)

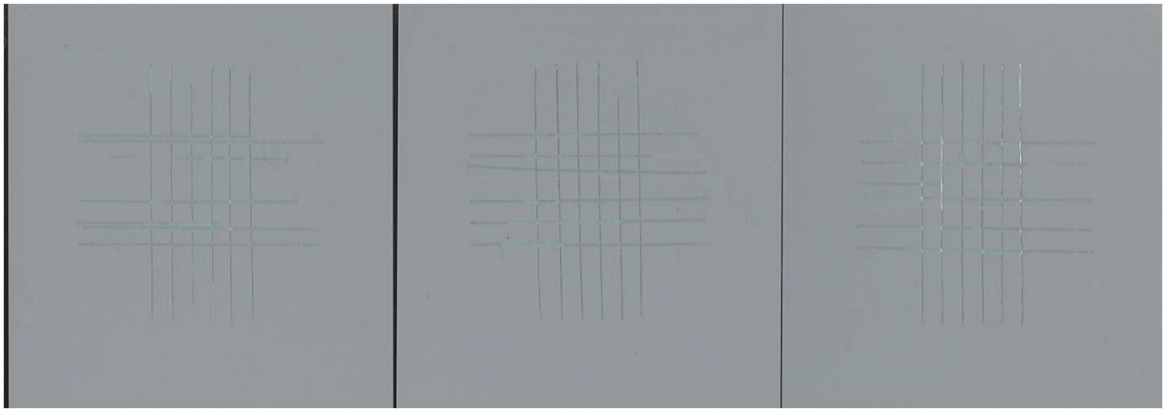


**Figure 61**: AA2024-T3 SurTec 650 + 23377N + 85285 (ASTM D3359, Method B)

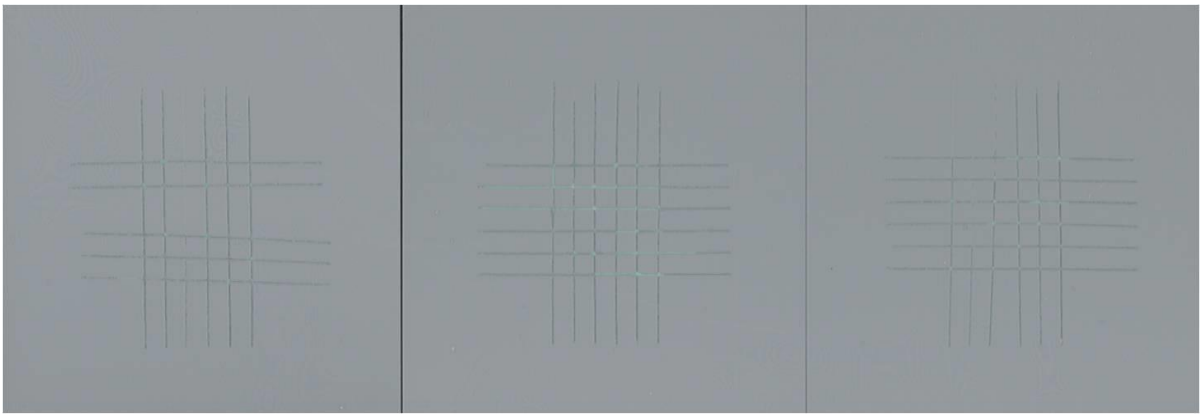


**Figure 62**: AA7075-T6 SurTec 650 + 23377N + 85285 (ASTM D3359, Method B)

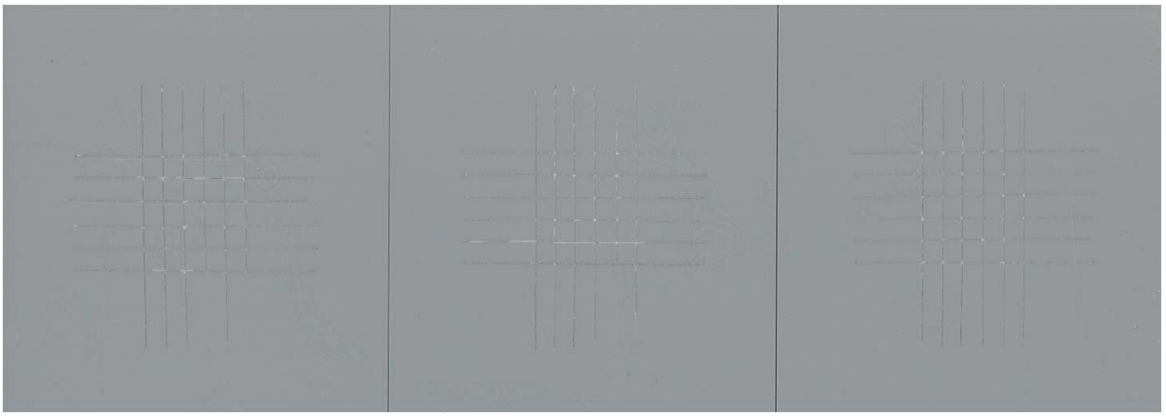


**Figure 63**: AA2024-T3 SurTec 650 + Crosslink + 85285 (ASTM D3359, Method B)

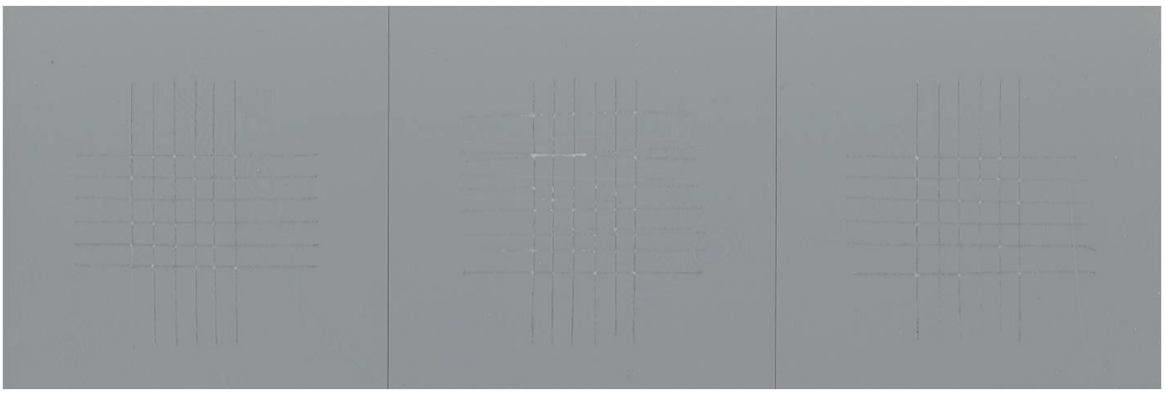


**Figure 64**: AA7075-T6 SurTec 650 + Crosslink + 85285 (ASTM D3359, Method B)

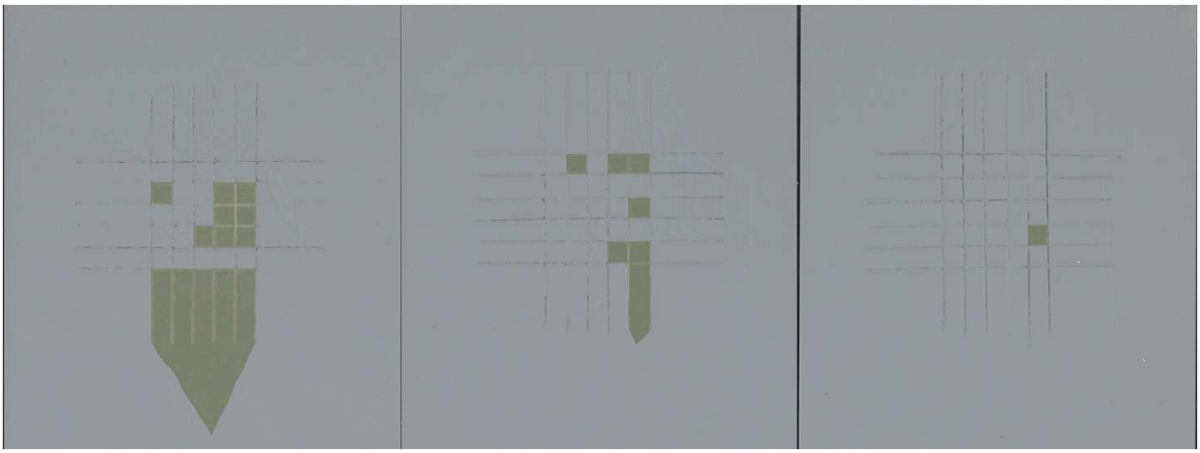


**Figure 65**: AA2024-T3 Alodine 1200S + 23377C + 85285 (ASTM D3359, Method B)

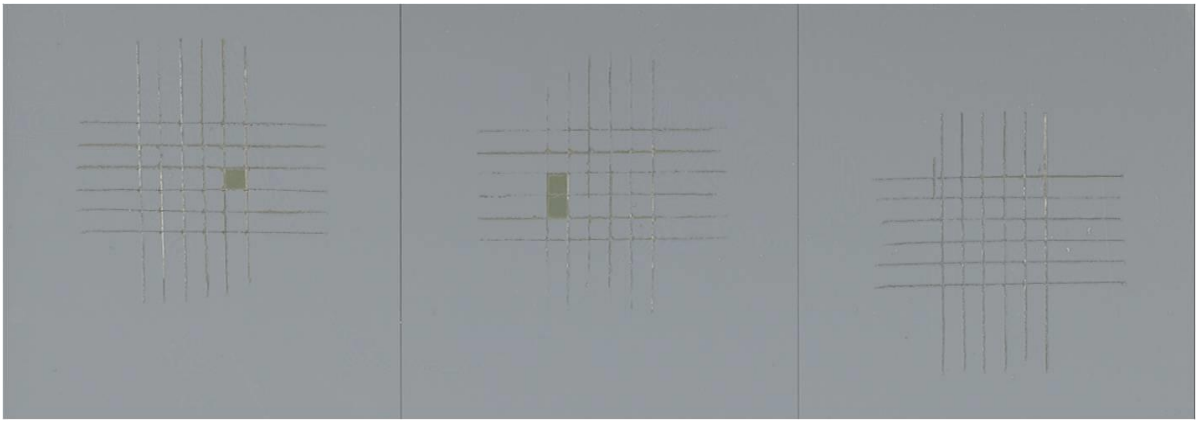


**Figure 66**: AA7075-T6 Alodine 1200S + 23377C + 85285 (ASTM D3359, Method B)

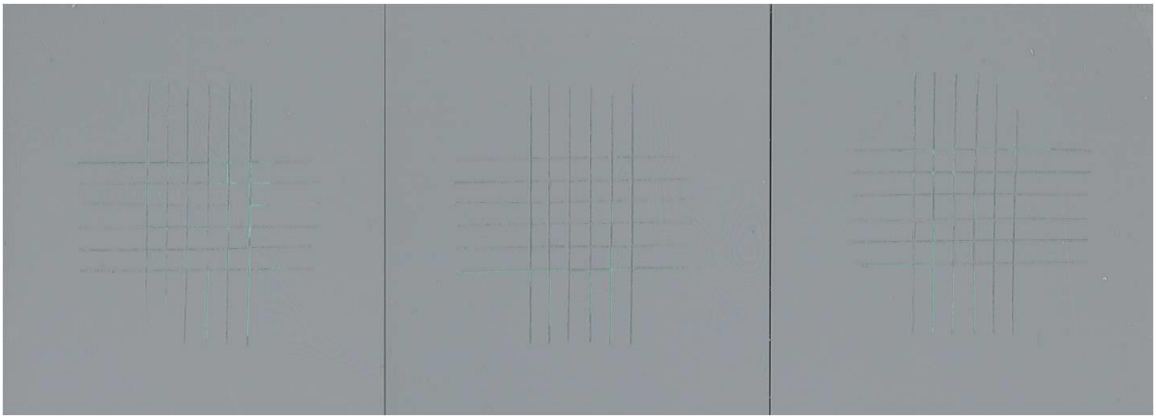


**Figure 67**: AA2024-T3 Alodine 1200S + 23377N + 85285 (ASTM D3359, Method B)

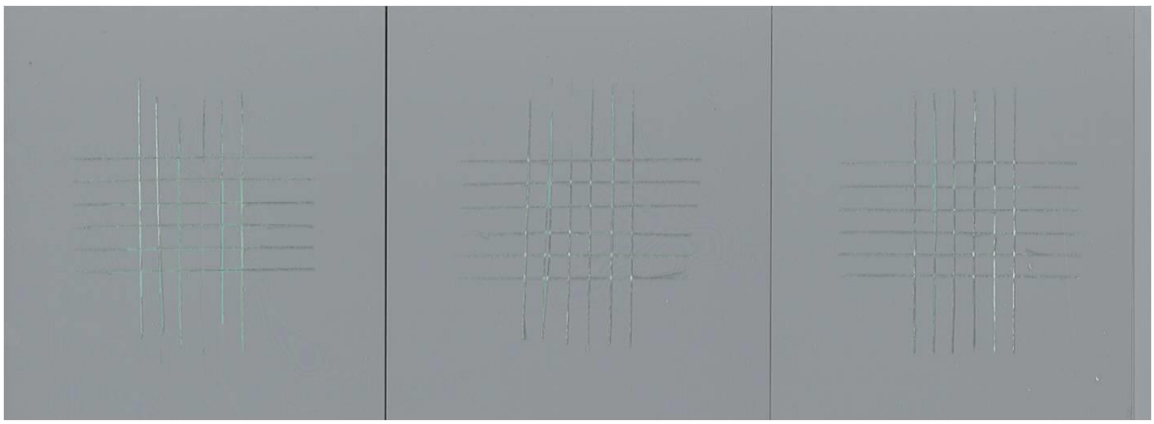


**Figure 68**: AA7075-T6 Alodine 1200S + 23377N + 85285 (ASTM D3359, Method B)

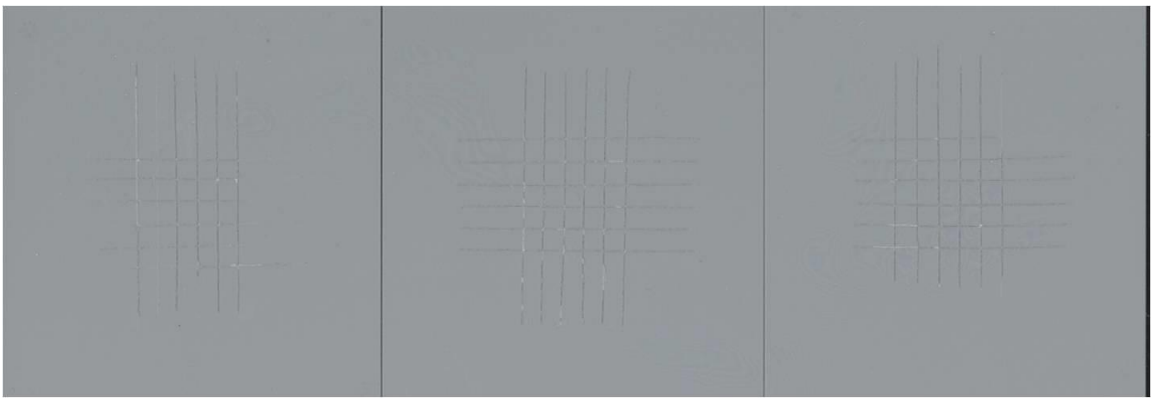


**Figure 69**: AA2024-T3 Alodine 1200S + Crosslink + 85285 (ASTM D3359, Method B)

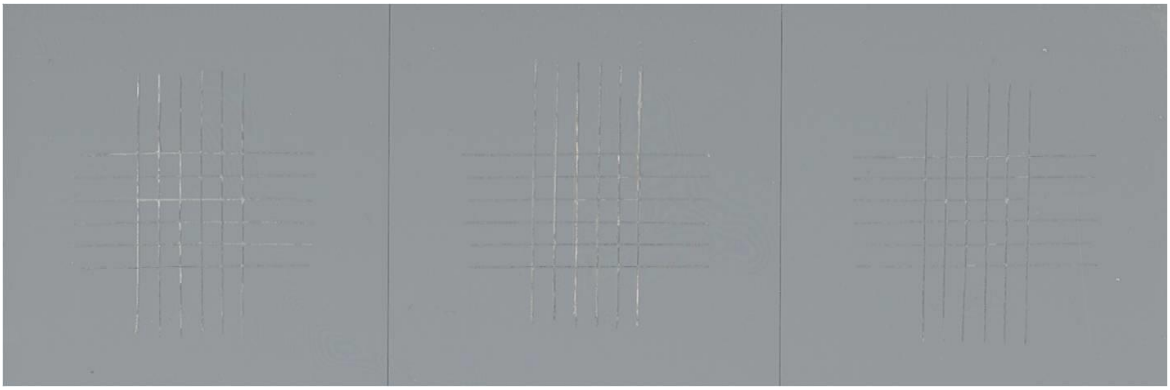


**Figure 70**: AA7075-T6 Alodine 1200S + Crosslink + 85285 (ASTM D3359, Method B)

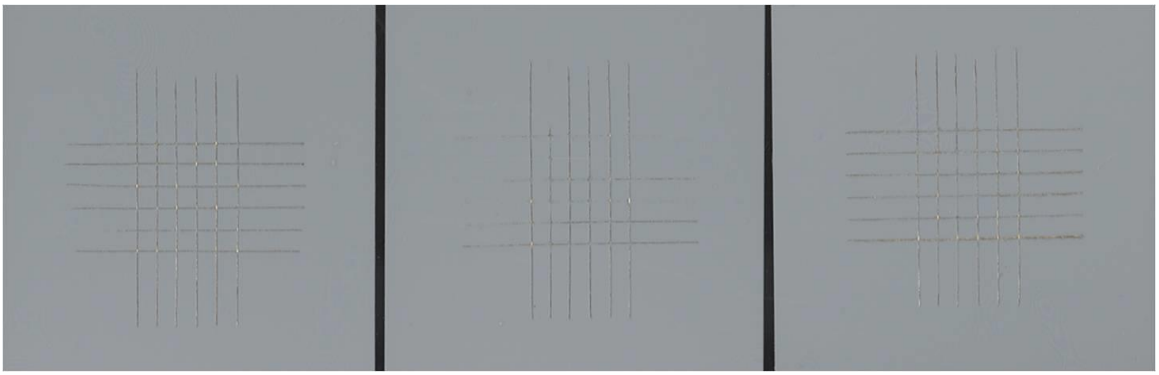


**Figure 71**: AA2024-T3 BAM-PPV + 23377C + 85285 (ASTM D3359, Method B)

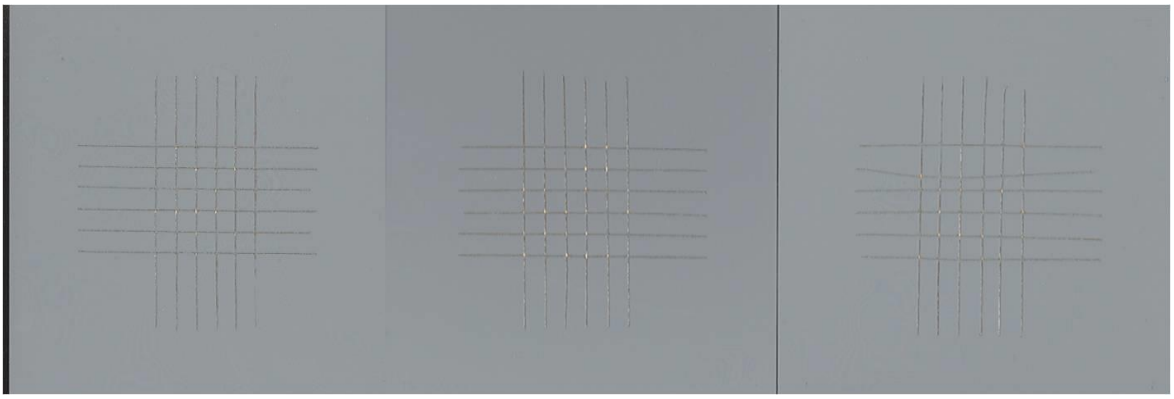


**Figure 72**: AA7075-T6 BAM-PPV + 23377C + 85285 (ASTM D3359, Method B)

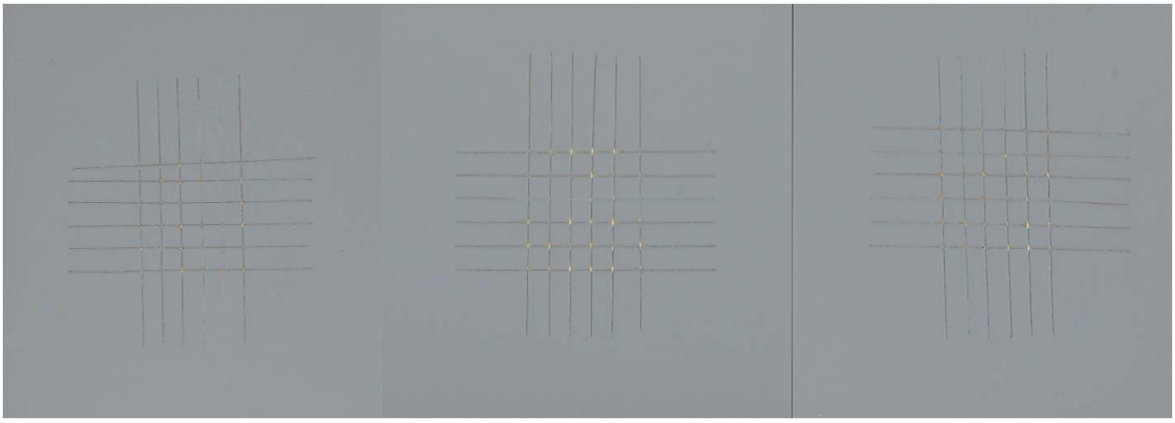


**Figure 73**: AA2024-T3 BAM-PPV + 23377N + 85285 (ASTM D3359, Method B)

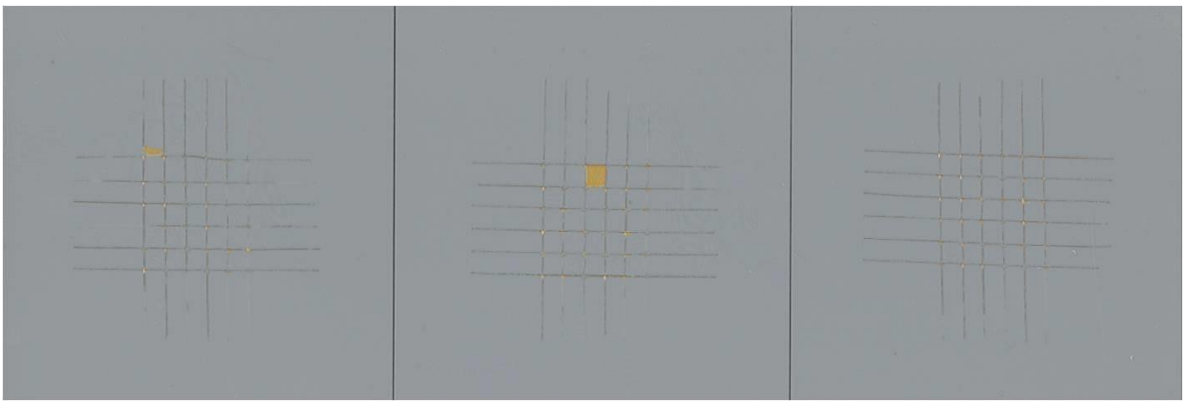


**Figure 74**: AA7075-T6 BAM-PPV + 23377N + 85285 (ASTM D3359, Method B)

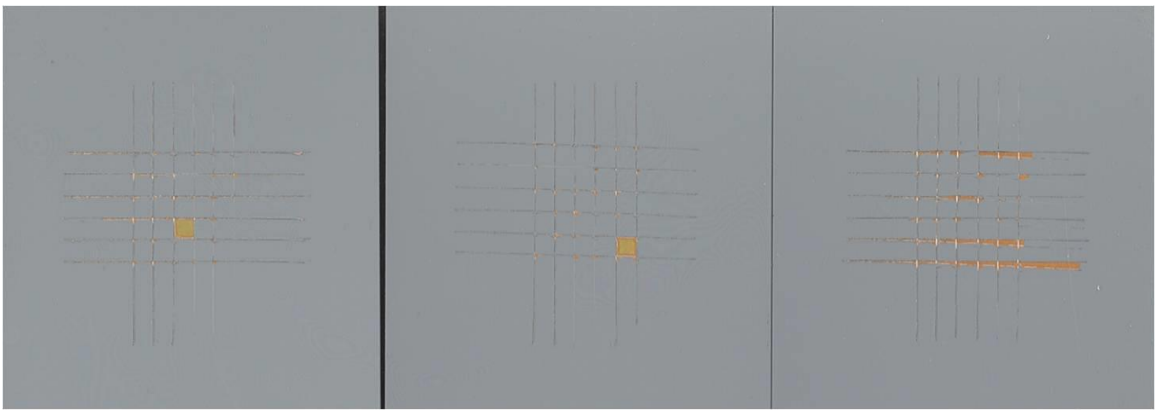


**Figure 75**: AA2024-T3 BAM-PPV + Crosslink + 85285 (ASTM D3359, Method B)

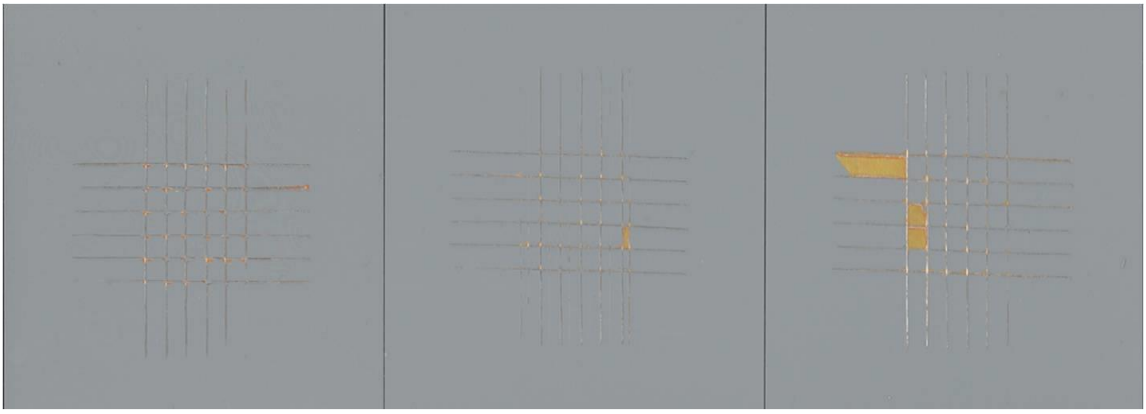


**Figure 76**: AA7075-T6 BAM-PPV + Crosslink + 85285 (ASTM D3359, Method B)

#### 4.1.3.1.2 Wet-tape Adhesion Testing of Crosslink Primer Systems

The wet-tape adhesion test is designed to measure inter-coat adhesion of an organic coating immersed in water for a short period of time. This test was performed in accordance with Federal Test Method Standard 141D, Method 6301, ASTM D 3359, Method A was used for adhesion rating. The wet adhesion data is shown in Figure 77 and

the majority of Crosslink test panels did not demonstrate acceptable adhesion behavior. Figures 78-95 show the results of the wet-tape adhesion testing.

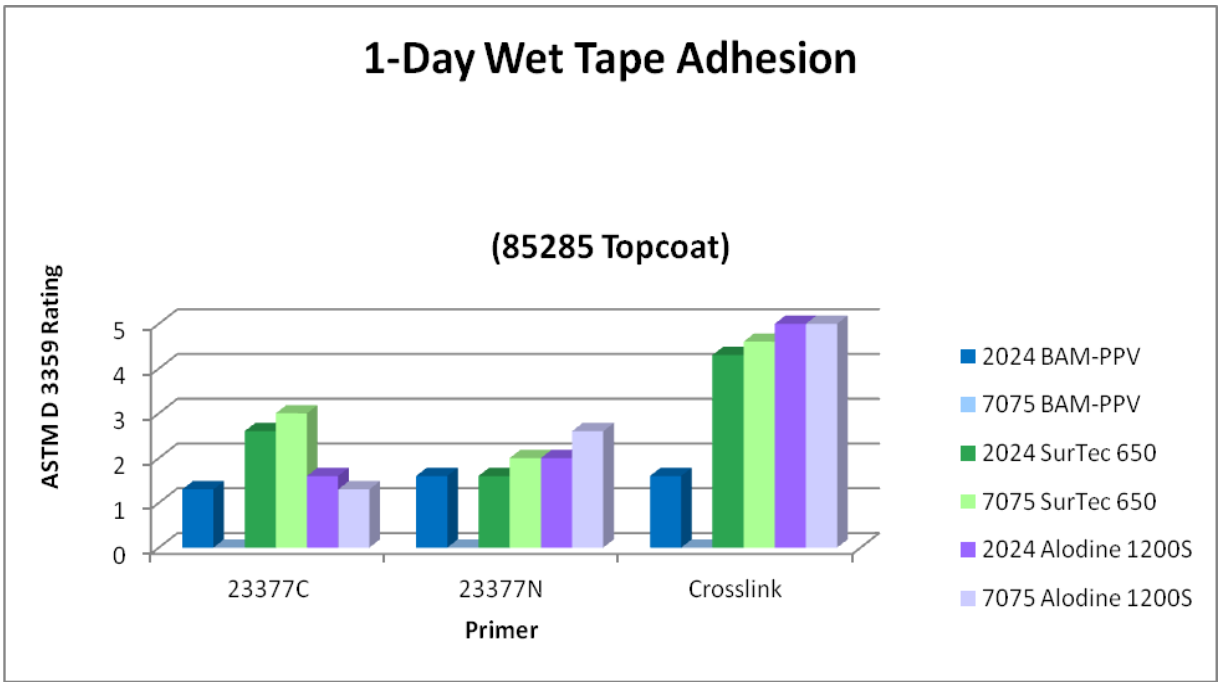



**Figure 77**: Wet Tape Adhesion Results per ASTM D 3359

**Figure 78**: AA2024-T3 SurTec 650 + 23377C + 85285 (1-Day Wet Adhesion)

**Figure 79**: AA7075-T6 SurTec 650 + 23377C + 85285 (1-Day Wet Adhesion)

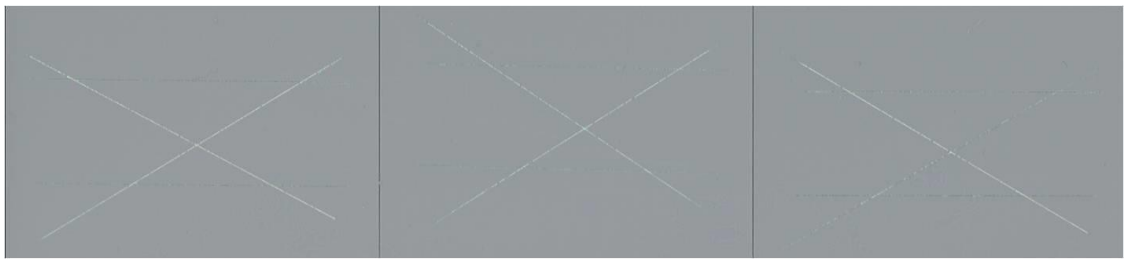


**Figure 80**: AA2024-T3 SurTec 650 + 23377N + 85285 (1-Day Wet Adhesion)

**Figure 81**: AA7075-T6 SurTec 650 + 23377N + 85285 (1-Day Wet Adhesion)

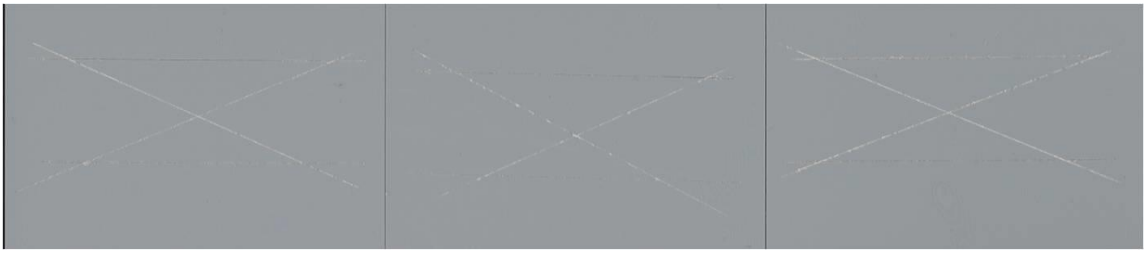


**Figure 82**: AA2024-T3 SurTec 650 + Crosslink + 85285 (1-Day Wet Adhesion)

**Figure 83**: AA7075-T6 SurTec 650 + Crosslink + 85285 (1-Day Wet Adhesion)

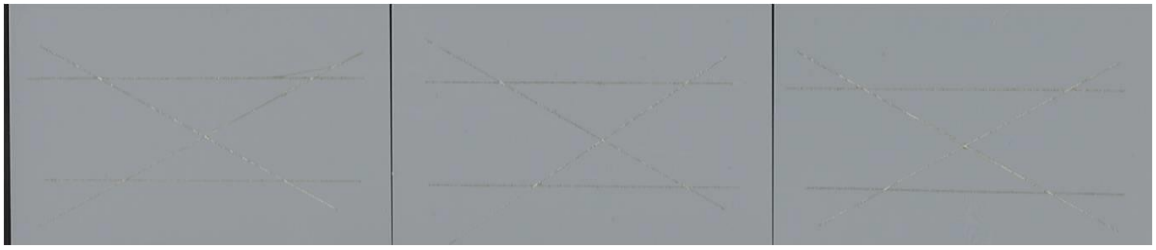


**Figure 84**: AA2024-T3 Alodine 1200S + 23377C + 85285 (1-Day Wet Adhesion)

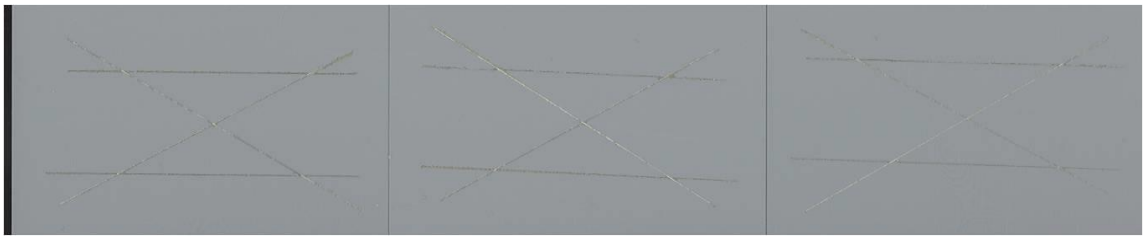


**Figure 85**: AA7075-T6 Alodine 1200S + 23377C + 85285 (1-Day Wet Adhesion)

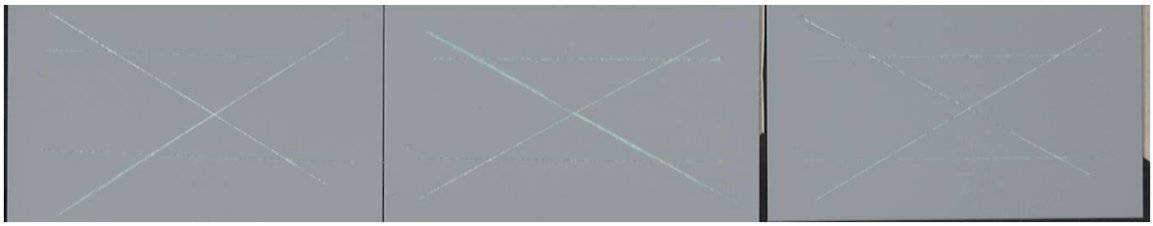


**Figure 86**: AA2024-T3 Alodine 1200S + 23377N + 85285 (1-Day Wet Adhesion)

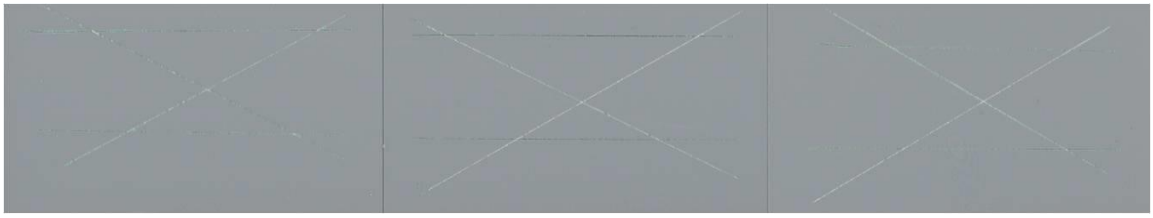


**Figure 87**: AA7075-T6 Alodine 1200S + 23377N + 85285 (1-Day Wet Adhesion)

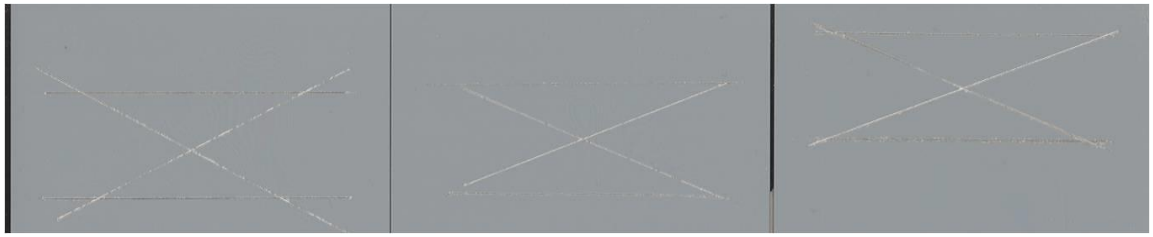


**Figure 88**: AA2024-T3 Alodine 1200S + Crosslink + 85285 (1-Day Wet Adhesion)

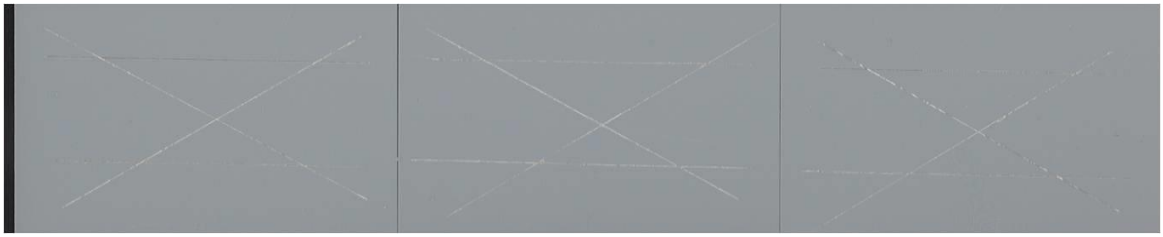


**Figure 89**: AA7075-T6 Alodine 1200S + Crosslink + 85285 (1-Day Wet Adhesion)

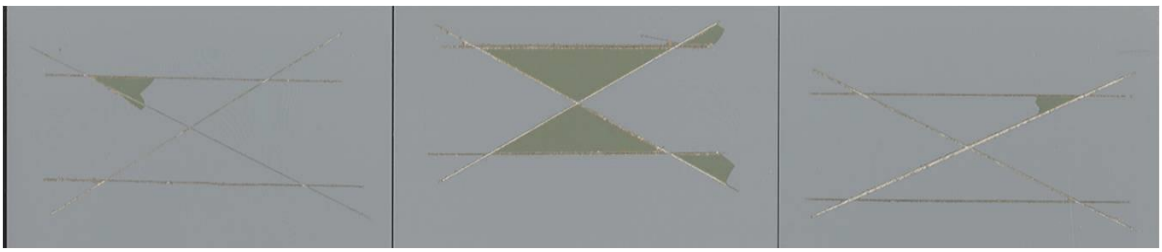


**Figure 90**: AA2024-T3 BAM-PPV + 23377C + 85285 (1-Day Wet Adhesion)

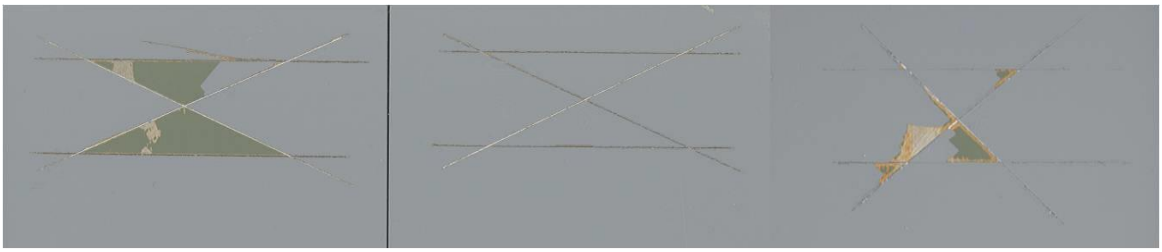


**Figure 91**: AA7075-T6 BAM-PPV + 23377C + 85285 (1-Day Wet Adhesion)

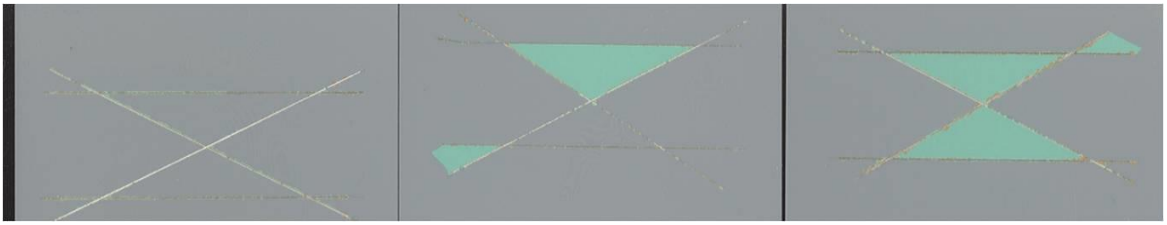


**Figure 92**: AA2024-T3 BAM-PPV + 23377N + 85285 (1-Day Wet Adhesion)

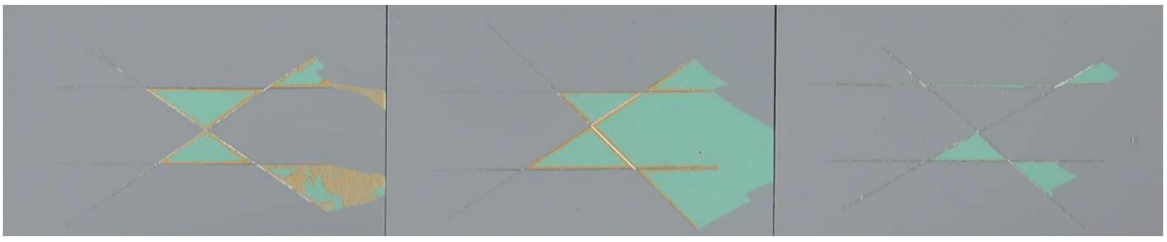


**Figure 93**: AA7075-T6 BAM-PPV + 23377N + 85285 (1-Day Wet Adhesion)

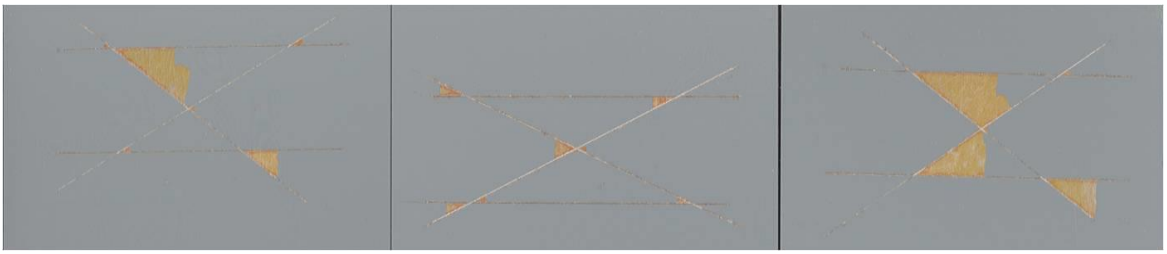


**Figure 94**: AA2024-T3 BAM-PPV + Crosslink + 85285 (1-Day Wet Adhesion)

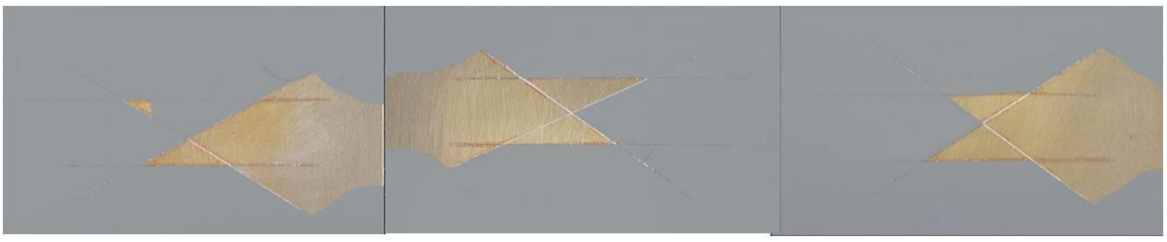


**Figure 95**: AA7075-T6 BAM-PPV + Crosslink + 85285 (1-Day Wet Adhesion)

#### 4.1.3.2 Accelerated Weathering Studies of Crosslink Primer System

The Crosslink primer systems were exposed to various accelerated weathering tests after adhesion studies were completed. Neutral salt spray exposure, $SO_2$ spray and filiform testing were performed on the Crosslink primer systems and evaluated.

##### 4.1.3.2.1 Neutral Salt Spray Testing

Neutral salt spray (NSS) exposure testing was performed to evaluate the ability of the Crosslink coating systems to withstand a 5-weight percent sodium chloride solution, pH-adjusted to a range of 6.5 – 7.2. This test was performed on both AA 2024-T3 and AA 7075-T6 substrates in accordance with ASTM B 117, except that the significant surface was inclined to 6° from the vertical. There were five replicates per coating system and each test coupon was scribed with an X-scribe (full size), exposed for 3000 hours, and checked for blistering, loss of adhesion, undercutting, pitting, and corrosion build-up within the scribe.

The rating system used on the test panels exposed to NSS is given in Section 3.1.2. The Crosslink test panels were evaluated and photographed after 3000 hours of exposure to neutral salt spray testing. Both NAWCAD and NAWCWD tested the Crosslink primer coating systems in NSS chambers and found similar performance results.

After examination, the test panels were assigned either pass, low and poor ratings. A complete description of the rating systems used for Tables 44 and 45 are found in Tables 6, 7 and 8. Listed below are a brief review of the rating system used to describe appearance, corrosion (1st number), undercutting (2nd number) and blistering (3rd number).

- Coating systems with no more than minor corrosion in the scribe (rating 0 – 1) received a “pass” rating.
- All coating systems with little undercutting (rating 0 – 2) received a “low” rating.
- Coating systems with greater amounts of corrosion in the scribe and undercutting, or those with blistering received a “poor” rating.

The ratings for NSS testing are shown in Table 44 and photodocumentation of the NSS test panels are shown in Figures 96-112.

**Table 44**: NSS ASTM B117 Test Results

| Coating System with 85285 Topcoat | AA2024-T3 5 Panel Ratings | Pass/Low/ Poor (2024-T3) | AA7075-T6 5 Panel Ratings | Pass/Low/ Poor (7075-T6) |
|---|---|---|---|---|
| Alodine 1200S + 23377C | 2 0 0<br>1 0 0<br>2 0 0<br>1 0 0<br>1 0 0 | **Pass** | 2 0 0<br>2 0 0<br>2 0 0<br>3 0 0<br>3 0 0 | **Low** |
| Alodine 1200S + 23377N | 4 0 0<br>4 0 0<br>5 0 0<br>4 0 0<br>4 0 0 | **Poor** | 5 0 0<br>5 0 0<br>5 0 0<br>5 0 0<br>4 0 0 | **Poor** |
| Alodine 1200S + Crosslink | 3 0 0<br>4 0 0<br>5 0 0<br>5 0 0<br>5 0 0 | **Poor** | 3 0 0<br>3 0 0<br>5 1 0<br>3 0 0<br>3 0 0 | **Poor** |
| SurTec 650 + 23377C | 0 0 0<br>1 0 0<br>1 0 0<br>1 0 0<br>2 0 0 | **Pass** | 1 0 0<br>1 0 0<br>1 0 0<br>3 0 0<br>2 0 0 | **Low** |
| SurTec 650 + 23377N | 5 0 0<br>4 0 0<br>4 0 0<br>5 0 0<br>5 0 0 | **Poor** | 5 0 0<br>5 0 0<br>5 0 0<br>5 0 0<br>5 0 0 | **Poor** |
| SurTec 650 + Crosslink | 5 0 0<br>4 0 0<br>5 0 0<br>5 1 0<br>5 1 0 | **Poor** | 5 1 0<br>5 1 0<br>3 1 0<br>5 1 0<br>4 1 0 | **Poor** |
| BAM-PPV + 23377C | 1 0 0<br>2 0 0<br>2 0 0<br>2 0 0<br>1 0 0 | **Pass** | 2 0 0<br>1 0 0<br>1 0 0<br>2 0 0<br>1 0 0 | **Pass** |
| BAM-PPV + 23377N | 5 5 0<br>5 4 0<br>5 3 0<br>5 4 5<br>5 4 0 | **Poor** | 5 5 1<br>5 3 0<br>5 4 0<br>5 4 0<br>5 4 0 | **Poor** |
| BAM-PPV + Crosslink | 5 4 0<br>5 5 0<br>5 4 0<br>4 4 0<br>5 1 0 | **Poor** | 4 5 0<br>5 5 0<br>5 5 0<br>5 5 0<br>5 5 0 | **Poor** |

**Figure 96**: AA2024-T3 Alodine 1200S + 23377C + 85285 (3000 hours NSS)

**Figure 97**: AA7075-T6 Alodine 1200S + 23377C + 85285 (3000 hours NSS)

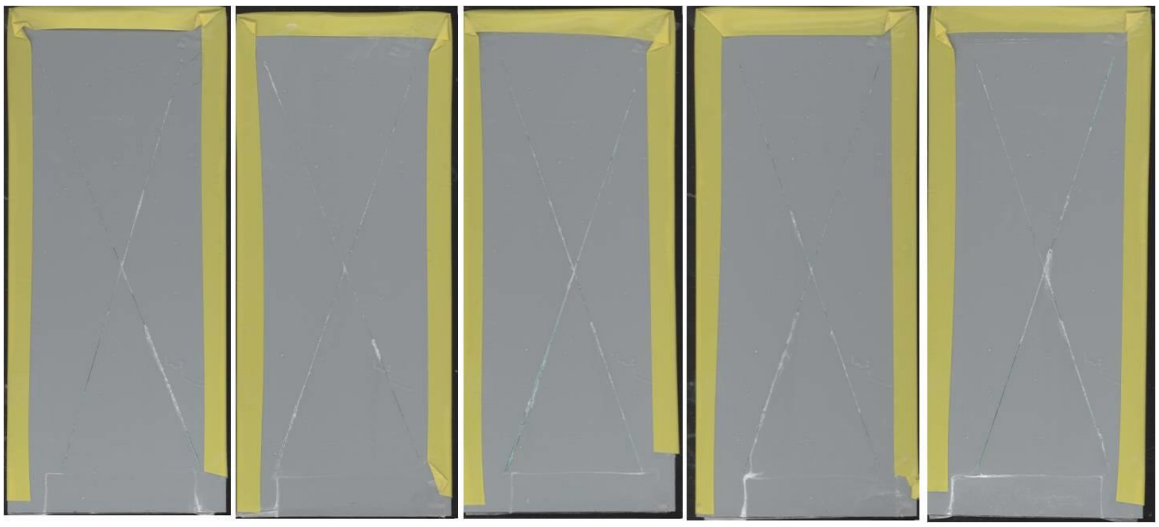


**Figure 98**: AA2024-T3 Alodine 1200S + 23377N + 85285 (3000 hours NSS)

**Figure 99**: AA7075-T6 Alodine 1200S + 23377N + 85285 (3000 hours NSS)

**Figure 100**: AA2024-T3 Alodine 1200S + Crosslink + 85285 (3000 hours NSS)

**Figure 101**: AA7075-T6 Alodine 1200S + Crosslink + 85285 (3000 hours NSS)

**Figure 102**: AA2024-T3 BAM-PPV + 23377C + 85285 (3000 hours NSS)

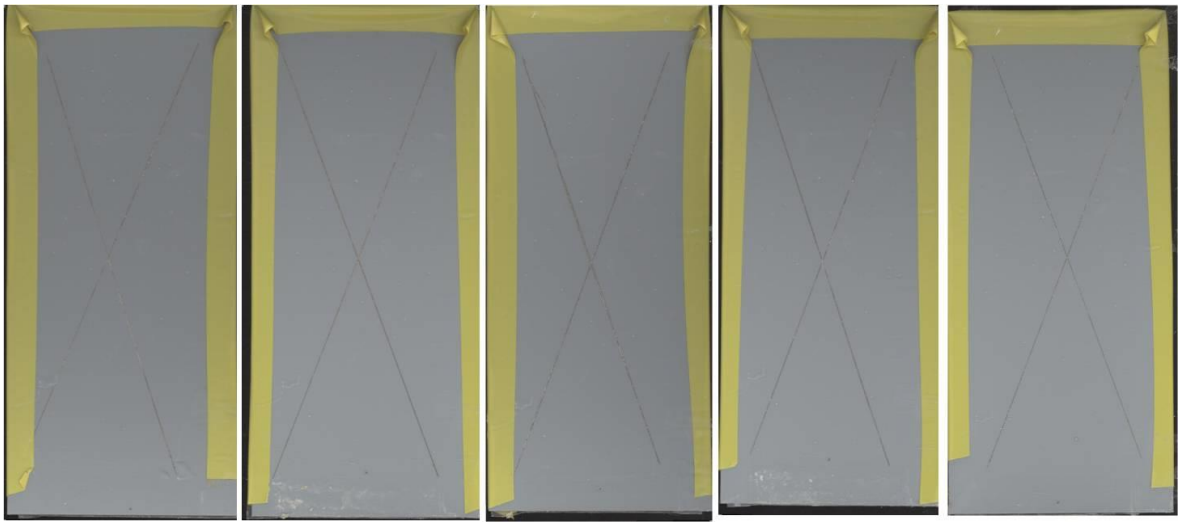


**Figure 103**: AA2024-T3 BAM-PPV + 23377N + 85285 (3000 hours NSS)

**Figure 104**: AA7075-T6 BAM-PPV + 23377N + 85285 (3000 hours NSS)

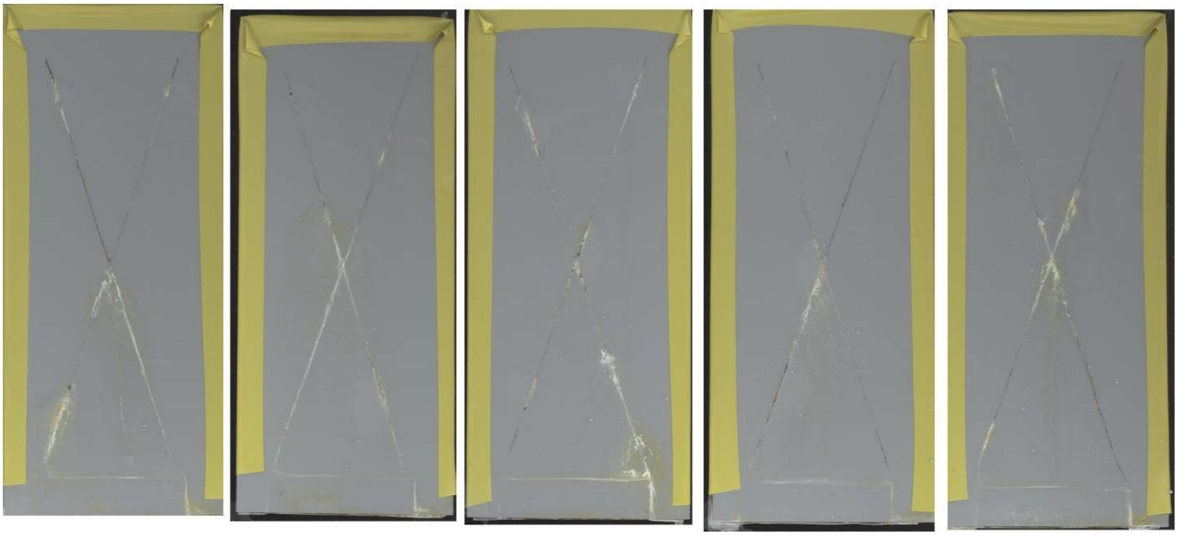


**Figure 105**: AA2024-T3 BAM-PPV + Crosslink + 85285 (3000 hours NSS)

**Figure 106**: AA7075-T6 BAM-PPV + Crosslink + 85285 (3000 hours NSS)

**Figure 107**: AA2024-T3 SurTec 650 + 23377C + 85285 (3000 hours NSS)

**Figure 108**: AA7075-T6 SurTec 650 + 23377C + 85285 (3000 hours NSS)

**Figure 109**: AA2024-T3 SurTec 650 + 23377N + 85285 (3000 hours NSS)

**Figure 110**: AA7075-T6 SurTec 650 + 23377N + 85285 (3000 hours NSS)

**Figure 111**: AA2024-T3 SurTec 650 + Crosslink + 85285 (3000 hours NSS)

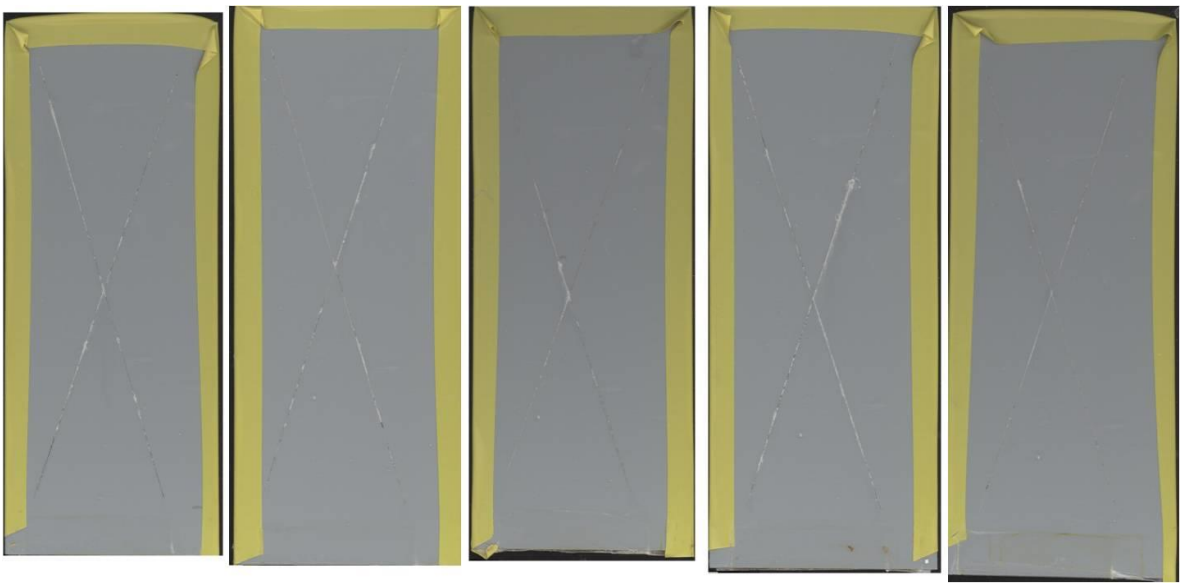


**Figure 112**: AA7075-T6 SurTec 650 + Crosslink + 85285 (3000 hours NSS)

#### 4.1.3.2.2 $SO_2$ Corrosion Testing

Cyclic sulfur dioxide salt fog exposure testing was performed on the Crosslink primer systems with control coupons to evaluate the ability of the Crosslink coating systems to withstand a more corrosive environment similar to that of an aircraft carrier. Test panels were subjected to a 5% salt spray test with a periodic introduction of sulfur dioxide gas directly into the chamber in accordance with ASTM G 85, Annex 4. The sulfur dioxide gas was emitted into the test chamber for 1 hour every 6 hours (four times per day). All test panels were scribed with an X-scribe (full-size), exposed for 1500 hours, and checked for blistering, loss of adhesion, undercutting, pitting, and corrosion build-up within the scribe. The Crosslink test coupons and controls were rated according to methods described in Section 3.1.2.3 and the results documented in Table 45 and the photodocumentation of the results are shown in Figures 113-130.

**Table 45**: ASTM G85, Annex 4 Test Results

| Coating System with 85285 Topcoat | AA2024-T3 5 Panel Ratings | Pass/Low/ Poor (2024-T3) | AA7075-T6 5 Panel Ratings | Pass/Low/ Poor (7075-T6) |
|---|---|---|---|---|
| Alodine 1200S + 23377C | 2 0 0<br>2 0 0<br>2 2 0<br>2 2 0<br>2 1 0 | **Low** | 2 3 0<br>2 2 0<br>2 2 0<br>2 2 0<br>2 2 0 | **Poor** |
| Alodine 1200S + 23377N | 2 0 0<br>2 1 0<br>2 1 0<br>2 2 0<br>2 2 0 | **Low** | 2 2 0<br>2 2 0<br>2 2 0<br>2 2 0<br>2 2 0 | **Poor** |
| Alodine 1200S + Crosslink | 3 1 0<br>2 1 0<br>2 1 0<br>2 1 1<br>2 1 0 | **Poor** | 3 2 0<br>3 3 0<br>2 3 0<br>3 3 0<br>2 3 0 | **Poor** |
| SurTec 650 + 23377C | 2 0 0<br>2 0 0<br>2 0 0<br>2 0 0<br>2 1 0 | **Low** | 2 3 0<br>2 3 0<br>2 3 0<br>2 2 0<br>2 2 0 | **Poor** |
| SurTec 650 + 23377N | 2 3 0<br>2 3 0<br>2 3 0<br>2 3 0<br>2 3 0 | **Poor** | 2 3 0<br>2 3 0<br>2 3 0<br>2 3 0<br>2 3 0 | **Poor** |
| SurTec 650 + Crosslink | 3 1 0<br>3 0 0<br>3 0 0<br>3 0 0<br>3 1 0 | **Poor** | 3 3 0<br>3 3 0<br>3 3 0<br>3 3 0<br>3 3 0 | **Poor** |
| BAM-PPV + 23377C | 3 5 0<br>3 5 0<br>3 5 0<br>3 5 0<br>3 5 0 | **Poor** | 3 4 0<br>4 4 0<br>3 4 0<br>3 4 2<br>3 4 0 | **Poor** |
| BAM-PPV + 23377N | 3 5 0<br>4 5 0<br>2 5 0<br>2 4 0<br>2 5 0 | **Poor** | 3 4 1<br>3 4 0<br>3 4 0<br>3 4 1<br>3 4 0 | **Poor** |
| BAM-PPV + Crosslink | 3 5 1<br>3 5 1<br>3 5 1<br>4 5 1<br>3 5 1 | **Poor** | 5 5 1<br>5 4 0<br>5 5 0<br>5 4 0<br>5 4 0 | **Poor** |

**Figure 113**: AA2024-T3 Alodine 1200S + 23377C + 85285
(1500 hours ASTM G85, A4)

**Figure 114**: AA7075-T6 Alodine 1200S + 23377C + 85285
(1500 hours  ASTM G85, A4)

**Figure 115**: AA2024-T3 Alodine 1200S + 23377N + 85285
(1500 hours ASTM G85, A4)

**Figure 116**: AA7075-T6 Alodine 1200S + 23377N + 85285
(1500 hours ASTM G85, A4)

**Figure 117**: AA2024-T3 Alodine 1200S + Crosslink + 85285
(1500 hours ASTM G85, A4)

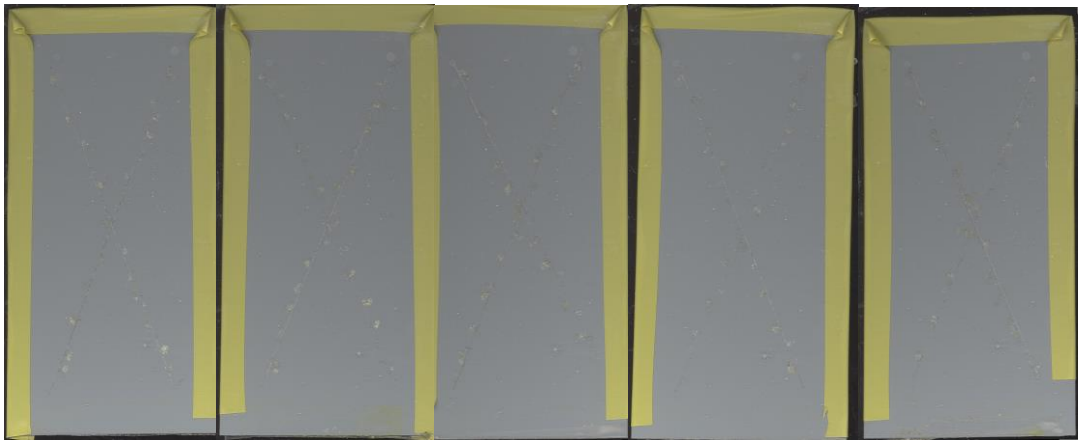


**Figure 118**: AA7075-T6 Alodine 1200S + Crosslink + 85285
(1500 hours ASTM G85, A4)

**Figure 119**: AA2024-T3 BAM-PPV + 23377C + 85285
(1500 hours ASTM G85, A4)

**Figure 120**: AA7075-T6 BAM-PPV + 23377C + 85285
(1500 hours ASTM G85, A4)

**Figure 121**: AA2024-T3 BAM-PPV + 23377N + 85285
(1500 hours ASTM G85, A4)

**Figure 122**: AA7075-T6 BAM-PPV + 23377N + 85285
(1500 hours ASTM G85, A4)

**Figure 123**: AA2024-T3 BAM-PPV + Crosslink + 85285
(1500 hours ASTM G85, A4)

**Figure 124**: AA7075-T6 BAM-PPV + Crosslink + 85285
(1500 hours ASTM G85, A4)

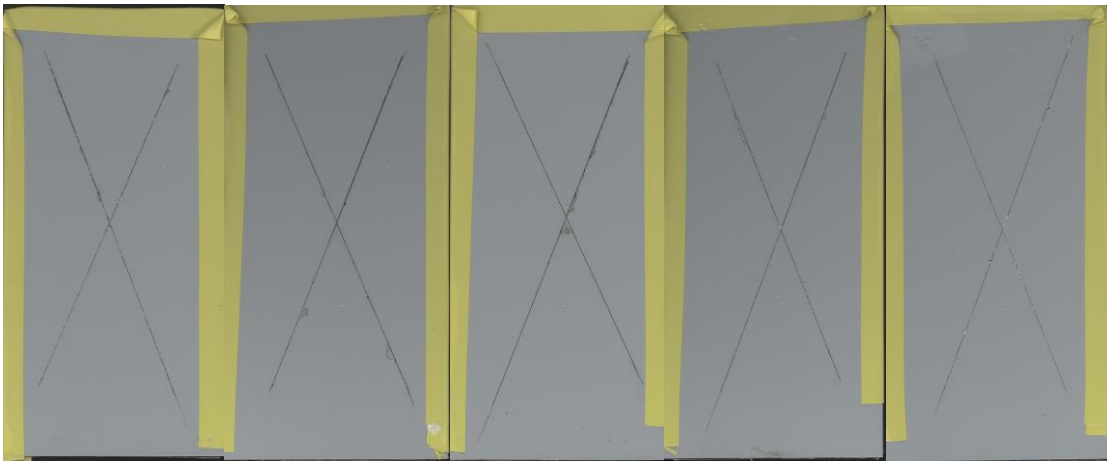


**Figure 125**: AA2024-T3 SurTec 650 + 23377C + 85285
(1500 hours ASTM G85, A4)

**Figure 126**: AA7075-T6 SurTec 650 + 23377C + 85285
(1500 hours ASTM G85, A4)

**Figure 127**: AA2024-T3 SurTec 650 + 23377N + 85285
(1500 hours ASTM G85, A4)

**Figure 128**: AA7075-T6 SurTec 650 + 23377N + 85285
(1500 hours ASTM G85, A4)

**Figure 129**: AA2024-T3 SurTec 650 + Crosslink + 85285
(1500 hours ASTM G85, A4)

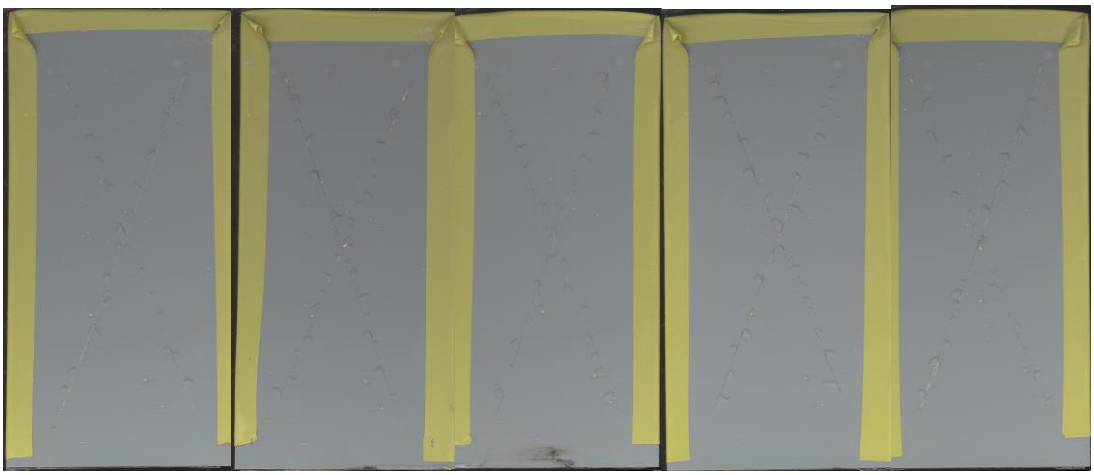


**Figure 130**: AA7075-T6 SurTec 650 + Crosslink + 85285
(1500 hours ASTM G85, A4)

#### 4.1.3.2.3 Filiform Testing

This test measures the ability of a coating system to protect the substrate against the formation of filiform corrosion and was performed in accordance with ASTM D 2803. The lengths of any thread-like filaments were measured at the end of the test duration and a rating of either pass/fail was assigned to the test panels. The results are summarized in Table 46 and photodocumentation of the coupons are found in figures 131-148.

**Table 46**: Filiform Testing Results per ASTM D 2803

| Alloy | Pretreatment | Primer | Pass (P)/Fail (F) |
|---|---|---|---|
| AA2024-T3 | Alodine 1200S | MIL-PRF-23377C | P P P P P |
| AA7075-T6 | Alodine 1200S | MIL-PRF-23377C | P P P P P |
| AA2024-T3 | Alodine 1200S | MIL-PRF-23377N | P P P P P |
| AA7075-T6 | Alodine 1200S | MIL-PRF-23377N | P P P P P |
| AA2024-T3 | Alodine 1200S | Crosslink | P P P P P |
| AA7075-T6 | Alodine 1200S | Crosslink | P P P P P |
| AA2024-T3 | SurTec 650 | MIL-PRF-23377C | P P P P P |
| AA7075-T6 | SurTec 650 | MIL-PRF-23377C | P P P P P |
| AA2024-T3 | SurTec 650 | MIL-PRF-23377N | P P P P P |
| AA7075-T6 | SurTec 650 | MIL-PRF-23377N | P P P P P |
| AA2024-T3 | SurTec 650 | Crosslink | F F F F F |
| AA7075-T6 | SurTec 650 | Crosslink | F F P P P |
| AA2024-T3 | BAM-PPV | MIL-PRF-23377C | F F F F F |
| AA7075-T6 | BAM-PPV | MIL-PRF-23377C | F P P P F |
| AA2024-T3 | BAM-PPV | MIL-PRF-23377N | F F F F F |
| AA7075-T6 | BAM-PPV | MIL-PRF-23377N | P P P P F |
| AA2024-T3 | BAM-PPV | Crosslink | F F F F F |
| AA7075-T6 | BAM-PPV | Crosslink | F P F P P |

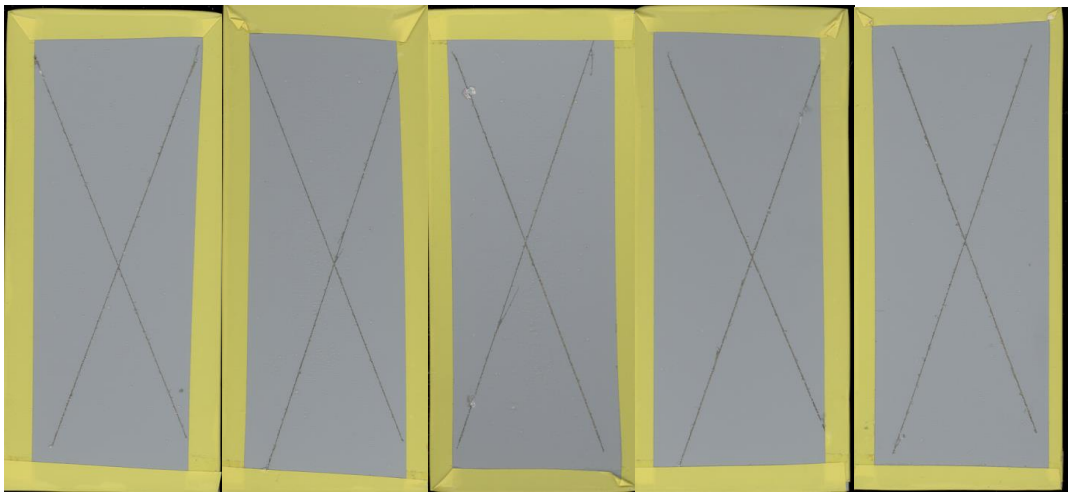


**Figure 131**: AA2024-T3 Alodine 1200S + 23377C + 85285 (ASTM D 2803)

**Figure 132**: AA7075-T6 Alodine 1200S + 23377C + 85285 (ASTM D 2803)

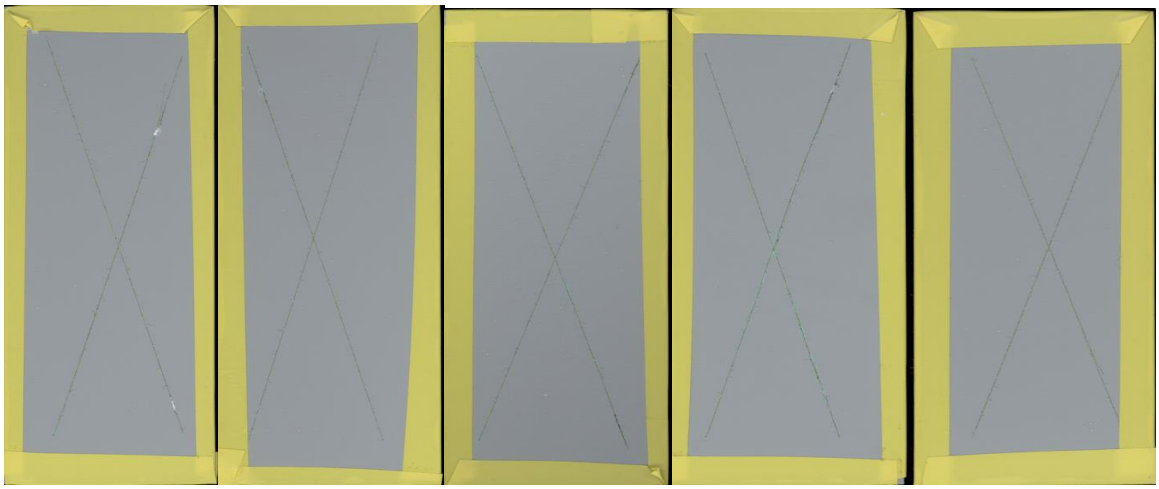


**Figure 133**: AA2024-T3 Alodine 1200S + 23377N + 85285 (ASTM D 2803)

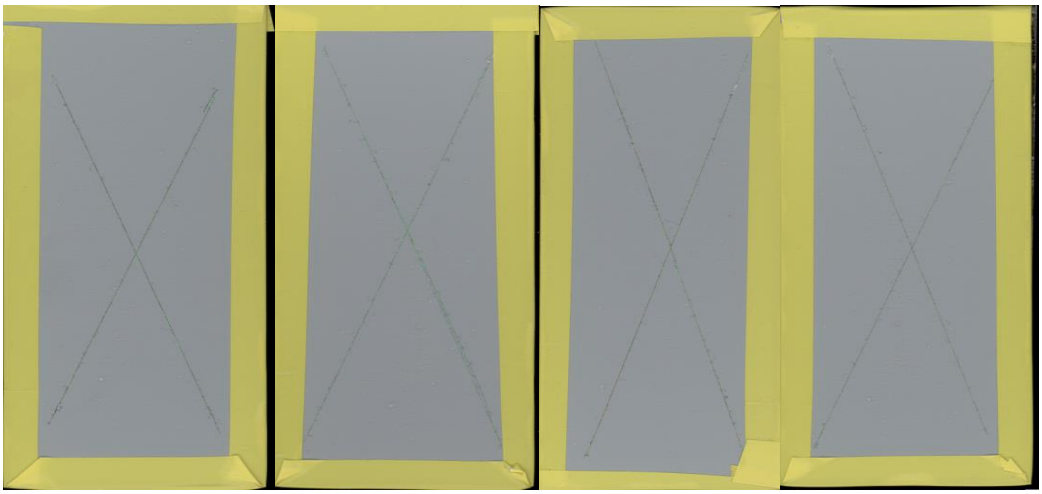


**Figure 134**: AA7075-T6 Alodine 1200S + 23377N + 85285 (ASTM D 2803)

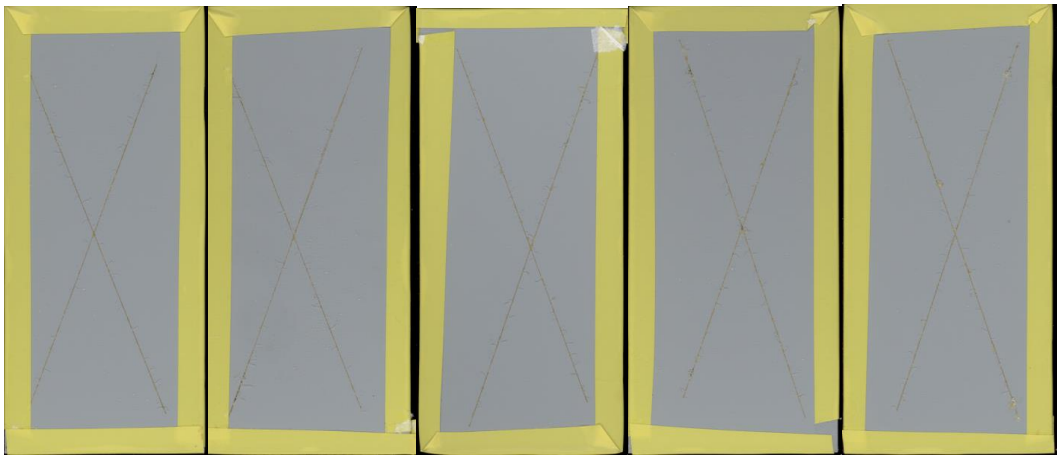


**Figure 135**: AA2024-T3 Alodine 1200S + Crosslink + 85285 (ASTM D 2803)

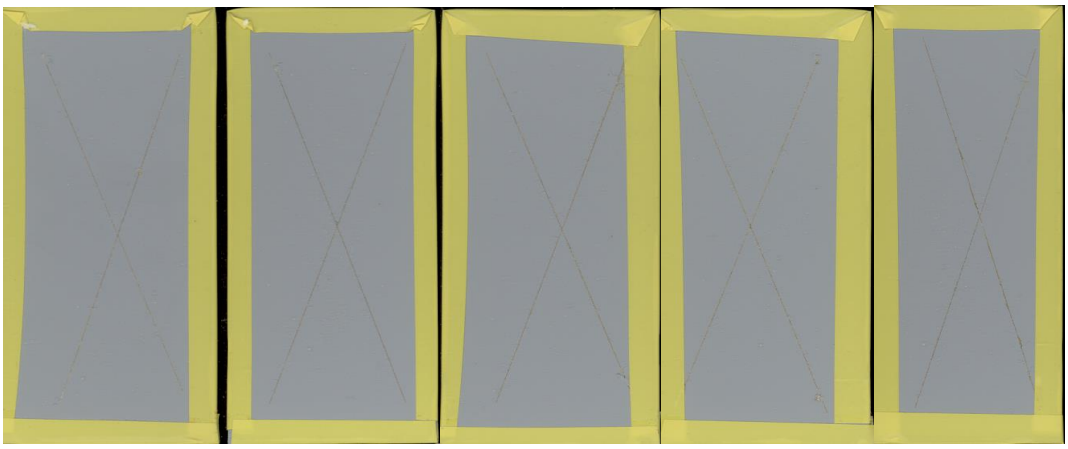


**Figure 136**: AA7075-T6 Alodine 1200S + Crosslink + 85285 (ASTM D 2803)

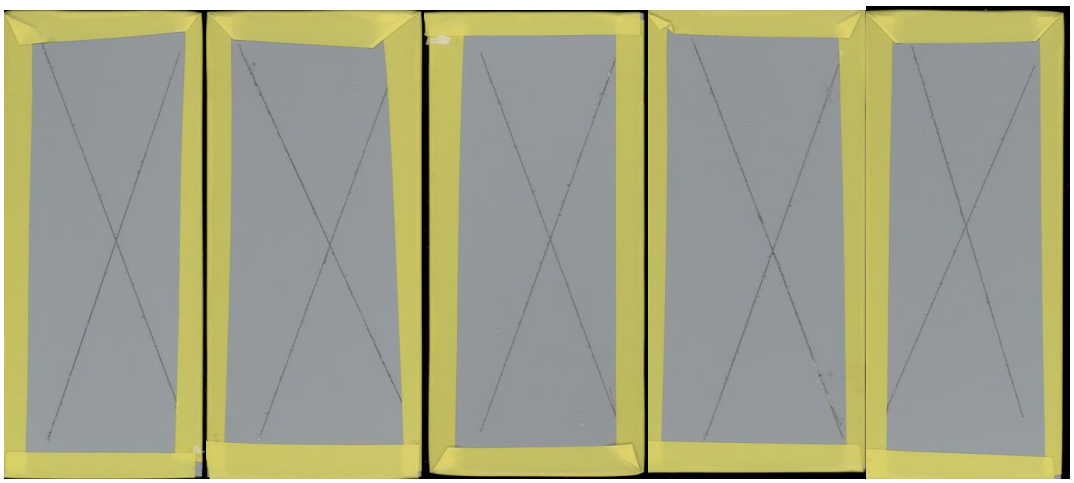


**Figure 137**: AA2024-T3 SurTec 650 + 23377C + 85285 (ASTM D 2803)

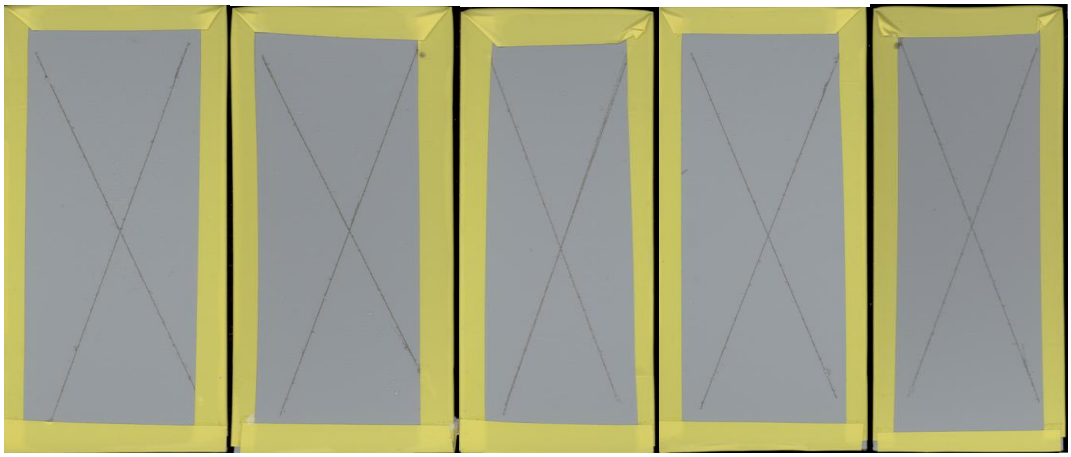


**Figure 138**: AA7075-T6 SurTec 650 + 23377C + 85285 (ASTM D 2803)

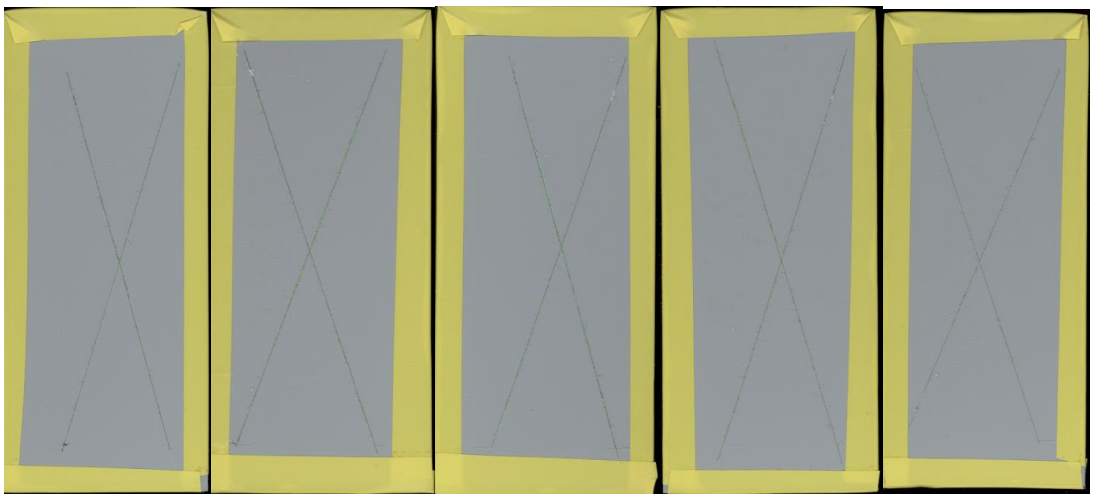


**Figure 139**: AA2024-T3 – SurTec 650 + 23377N + 85285 (ASTM D 2803)

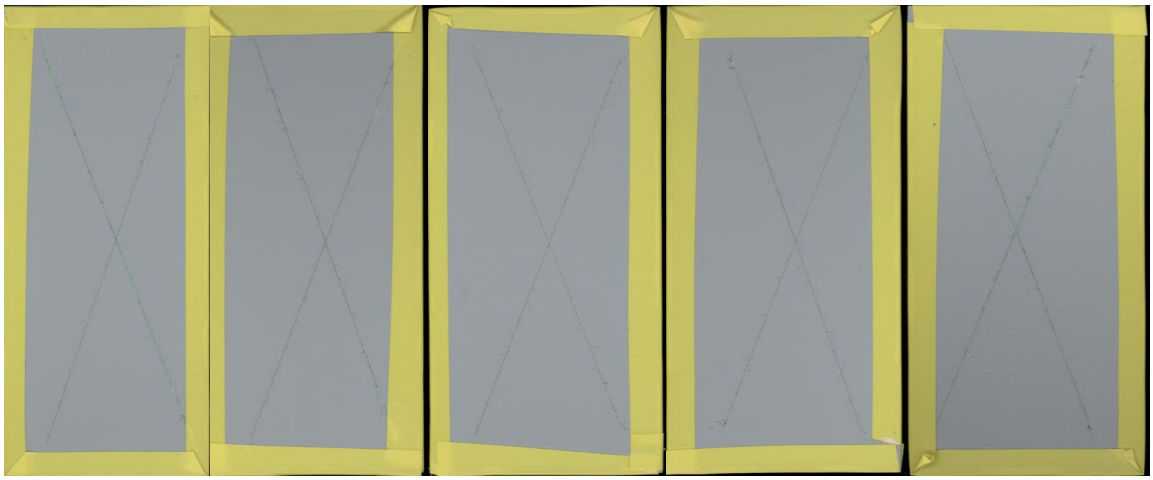


**Figure 140**: AA7075-T6 SurTec 650 + 23377N + 85285 (ASTM D 2803)

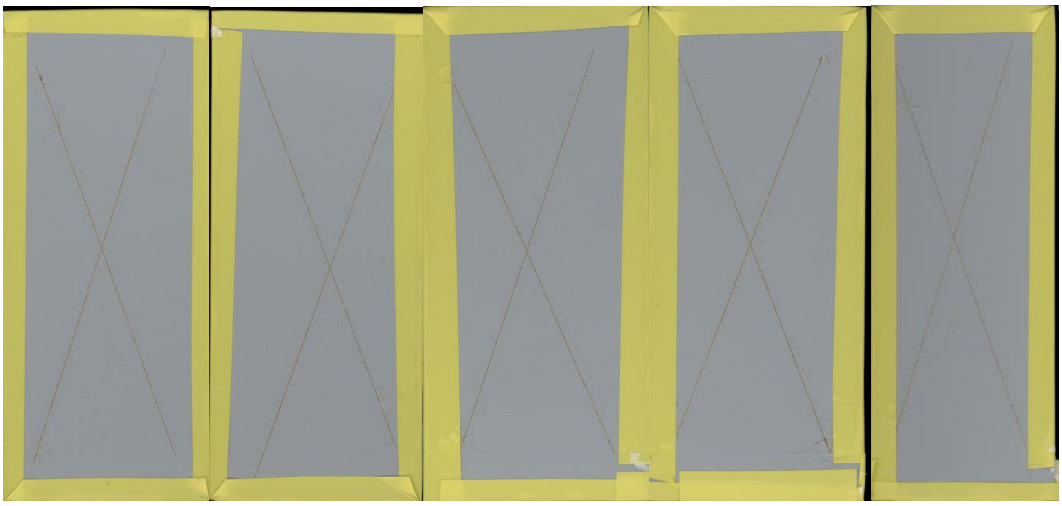


**Figure 141**: AA2024-T3 SurTec 650 + Crosslink + 85285 (ASTM D 2803)

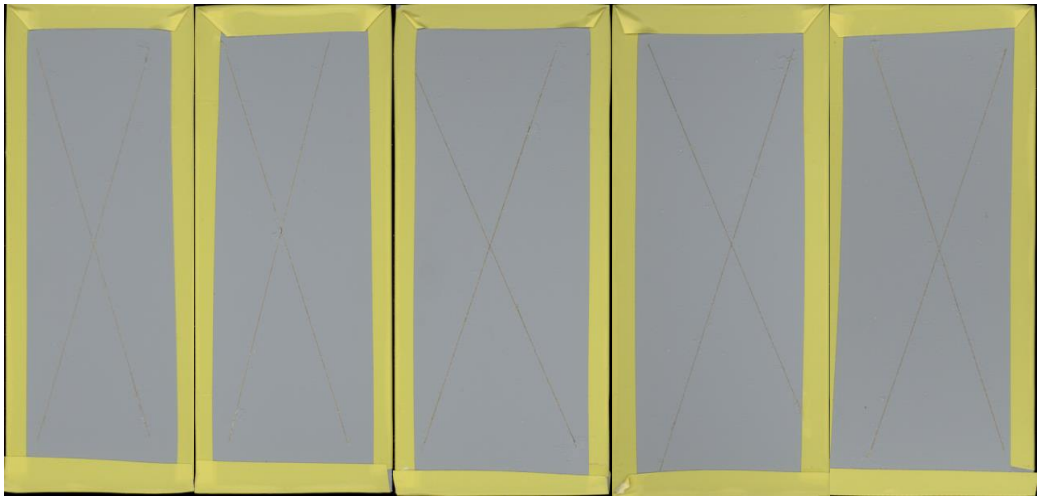


**Figure 142**: AA7075-T6 SurTec 650 + Crosslink + 85285 (ASTM D 2803)

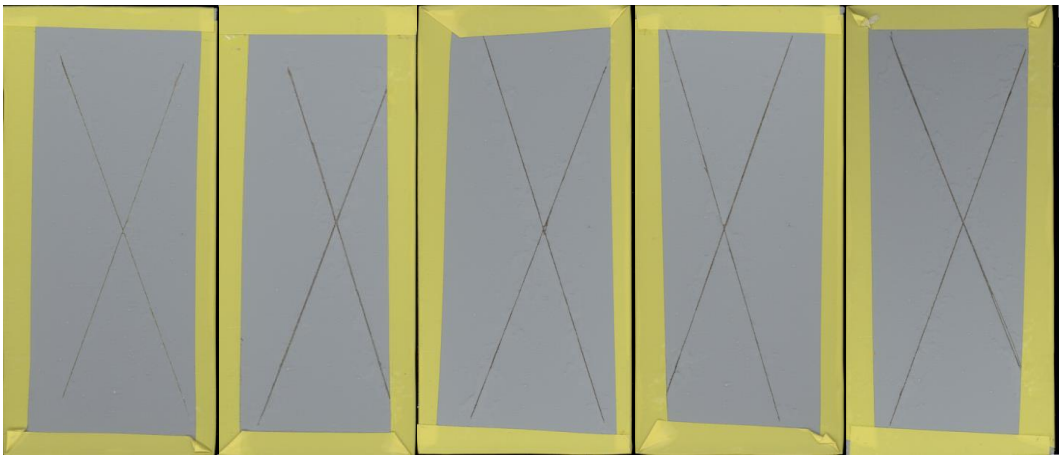


**Figure 143**: AA2024-T3 BAM-PPV + 23377C + 85285 (ASTM D 2803)

**Figure 144**: AA7075-T6 BAM-PPV + 23377C + 85285 (ASTM D 2803)

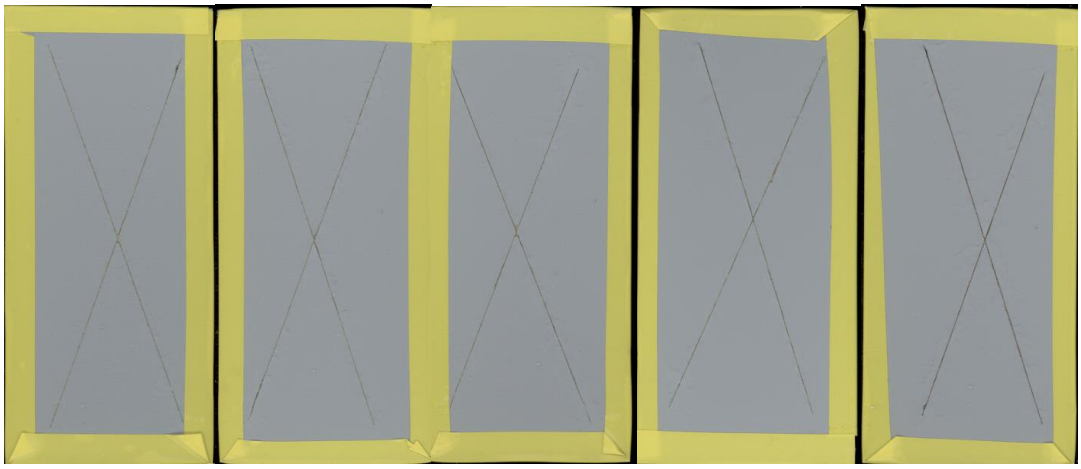


**Figure 145**: AA2024-T3 BAM-PPV + 23377N + 85285 (ASTM D 2803)

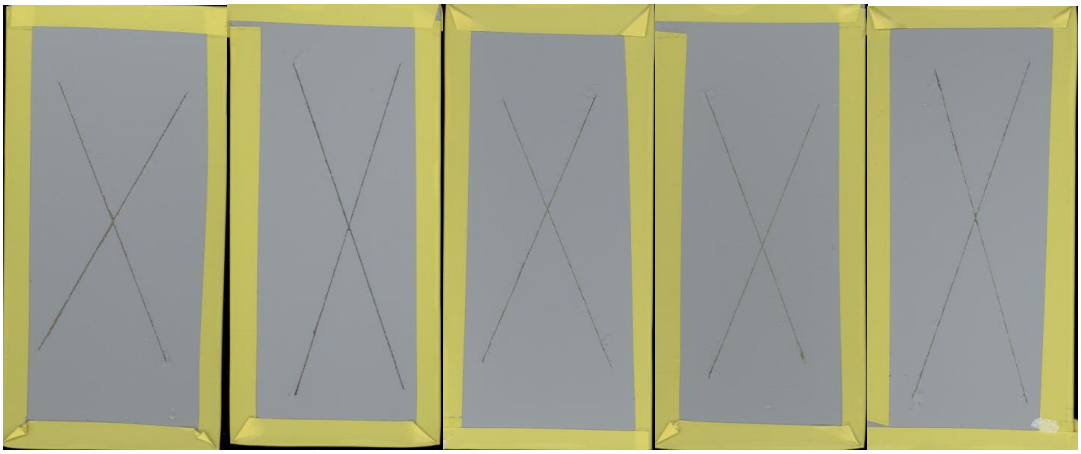


**Figure 146**: AA7075-T6 BAM-PPV + 23377N + 85285 (ASTM D 2803)

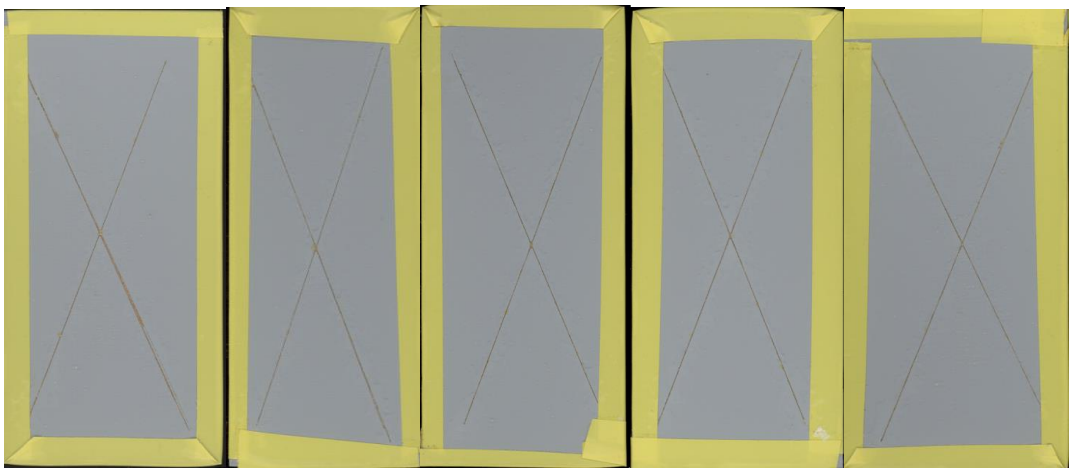


**Figure 147**: AA2024-T3 BAM-PPV + Crosslink + 85285 (ASTM D 2803)

**Figure 148**: AA7075-T6 BAM-PPV + Crosslink + 85285 (ASTM D 2803)

#### 4.1.3.3 Additional Testing for Crosslink Primer Systems

Fluid resistance measurements were taken on the Crosslink primer systems to determine any effect of aerospace fluids on this new primer system. The method used was described previously and the results are shown below in section 4.1.3.3.1.

##### 4.1.3.3.1 Fluid Resistance Testing for Crosslink Primer Systems

Fluid resistance testing is performed to determine what effect can be expected by common aerospace fluids that come in contact with organic coatings. Hydraulic fluid resistance tests were performed by immersing test panels in hydraulic fluid conforming to MIL-PRF-83282 for 24 hours at a fluid temperature of 150 ± 5 °F. The coating was observed after removal from the hydraulic fluid and examined for conformance to MIL-PRF-85285, Section 3.8.1. All test panels passed with none of the Crosslink primer coatings exhibiting any blistering, softening, or other coating defects (see Table 47).

**Table 47**: Fluid Resistance Testing of Crosslink Primer Systems

| Coating System with 85285 Topcoat | Pass/Fail (2024-T3) | Pass/Fail (7075-T6) |
|---|---|---|
| Alodine 1200S + 23377C | Pass | Pass |
| Alodine 1200S + 23377N | Pass | Pass |
| Alodine 1200S + Crosslink | Pass | Pass |
| SurTec 650 + 23377C | Pass | Pass |
| SurTec 650 + 23377N | Pass | Pass |
| SurTec 650 + Crosslink | Pass | Pass |
| BAM-PPV + 23377C | Pass | Pass |
| BAM-PPV + 23377N | Pass | Pass |
| BAM-PPV + Crosslink | Pass | Pass |

#### 4.1.3.4 NAWCWD/NAWCAD Conclusions for Crosslink Primer Systems

The results from the NAWCWD and NAWCAD showed similar performance of the Crosslink primer when compared to the results obtained from AF and Army testing. The Crosslink primer system performed the best in each service with a CCC and topcoat. Alternative pretreatments such as TCP, Prekote and BAM-PPV with the Crosslink primer with and without top coat showed poor performance.
The results from the NAWCWD and NAWCAD are summarized below in bullet form.

- Crosslink primer with various pretreatments, (CCC, TCP or BAM-PPV) and topcoat passed fluid resistance testing.
- Crosslink primer with CCC and topcoat passed dry adhesion.
- Crosslink primer with TCP or BAM-PPV pretreatment and topcoat failed dry tape adhesion.
- Crosslink primer with CCC and topcoat passed wet tape adhesion test.
- Crosslink primer with TCP or BAM-PPV pretreatment and topcoat failed wet tape adhesion test.
- Crosslink primer did not pass any NSS testing with any combination of pretreatment and topcoat as determined by NAWCAD and NAWCWD.
- Crosslink did not meet the minimum requirements for $SO_2$ or filiform testing showing poor performance with alternative pretreatments (TCP and BAM-PPV). The only passing coupons for filiform testing were the CCC + Crosslink primer + topcoat combination on both AA 2024-T3 and AA 7075-T6.

### 4.1.4 Laboratory Testing at Crosslink

#### 4.1.4.1 Materials and preparation for Crosslink Inhibitor

##### 4.1.4.1.1 Materials Used

Listed below is a materials list for the preparation of the Crosslink Corrosion Inhibitor ($Zn(DMcT)_2$:

- 260 grams DMcT (ASV) – Lot # 01342-03016-09 (65 grams per batch )
- 1080 gms Zinc Nitrate Hexahydrate reagent grade 98% (Sigma Aldrich) Lot # MKAA3272 (270 grams per batch )
- 19200 mL Methanol (Sigma Aldrich) HPLC grade 99.8% Lot # 79896TJ( 4800 mL per batch )
- 4800 mL filtered DI $H_2O$ *(Used DI $H_2O$ from R&D Bay)*
- 10g of dipotassium salt of DMcT ($C_2N_2S_3K_2$) Alfa Aesar (Lot USLF004036)

190 grams of filtered DI $H_2O$ to make a 5% by weight solution.

##### 4.1.4.1.2 General preparation of the Crosslink Inhibitor ($Zn(DMcT)_2$

The preparation of $Zn(DMcT)_2$ neutralized with Potassium DMcT was prepared at Crosslink using a patented process. The procedure is described below and represents the inhibitor that was tested by each service. This inhibitor formulation has undergone modifications during the course of this WP 200904 ESTCP Program and is currently under study for the NAWCAD WP-201132 “Comprehensive Evaluation and Transition of Non-Chromated Paint Primers.”

**The initial process begins with the precipitation step**:

1) In a four liter beaker, dissolve 65g of DMcT in 1800mL of methanol,
2) Use a stir bar and stir plate to speed up dissolution (approximately 20-30 minutes),
3) In a two liter beaker, dissolve 270g of $Zn(NO_3)_2 \cdot 6H_2O$ (Aldrich) in 1300mL of methanol (approximately 5-10 minutes),
4) After both compounds have dissolved in methanol, slowly add zinc nitrate solution to beaker containing DMcT solution (approximately 10 minutes). While adding zinc nitrate solution, maintain a high stirrer speed for DMcT solution. When addition of zinc nitrate solution is completed, decrease stir speed, cover beaker, and leave stirring for at least one hour. Remove from stirrer and was allowed to stand overnight.

**The second step in this process required a washing step**:

5) After overnight standing, carefully decant solvent from beaker. Remove as much solvent as possible without losing a significant amount of product (>1 gram).
6) Methanol wash: Transfer material to 2000 mL beaker. Add another 1500mL of methanol and place on stir plate for a few minutes, making sure that all precipitate is mixed back into solution. Stop stirring, allow precipitate to settle (will take ≈ 1 hour), then decant again. Repeat washing process with 1500mL of methanol again, then decant off methanol.
7) Water wash: Add 1200mL of filtered, DI water to precipitate and stir. Remove from stir plate, allow precipitate to sit overnight. After overnight standing, measure pH and decant water.

**The third step in this process required a grinding step**:

8) Remove precipitate and place in mill jar with media. Filtered DI water may be used to remove remainder of precipitate from beaker. The water will also be required to adjust the slurry viscosity for best grinding. The viscosity should be slightly thick, but not so thick that the media cannot move when the jar is rolled. This can be ascertained by placing the lid on the jar and rolling the jar across a bench top. If one can hear the media falling, then enough water has been added. Take care to not add excess water. If too much water has been added, allow precipitate to settle, and remove water with pipette.

9) Allow precipitate to grind for several hours, preferably overnight. Check grind with Hegman gauge. If grind is five or less, then continue grinding until a grind of five or greater is achieved.

10) Removing slurry from jar: Slurry should be thick. Used a glass funnel with a stem small enough to catch media but large enough to let material flow without impedance. Should not have to adjust viscosity; just use small amounts of DI water to rinse media and jar. Pour jar contents into funnel, place above a large beaker. Try to use a minimal amount of water. If product settles and leaves a large, clear layer of water, pour off the excess water.

**The fourth step of this process required a neutralization step**:

11) Weigh a polyethylene or polypropylene bottle that is large enough to hold all of the precipitate. Pour slurry into bottle and record weight of sample. Determine percent solids and calculate the amount of product recovered.

12) Prepare 50g of a 5% by weight solution of the dipotassium salt of DMcT ($K_2$DMcT) in filtered DI water.

Note: While making pH measurements, at **NO time** is the pH probe to be inserted into the contents of the bottle. The pH electrode is a potential source of chloride contamination. To measure pH, always remove a small sample (about 1 gram) of slurry, dilute with water, and then measure the pH of that sample. Discard the sample when finished, and do not place back in bottle.

13) Remove 1g of slurry and place in vial. Dilute with 9g of DI water. Measure pH. The pH should be somewhat acidic, around 4.5 to 5. Place vial on balance, lower pH probe into solution. Tare balance. Add 5% $K_2$DMcT solution to vial until pH is 7.0 – 7.5. Record the mass of $K_2$DMcT solution required for this. Multiply this number by the number of grams of product in bottle determined in step 10. This is approximately the amount of $K_2$DMcT solution required to neutralize the entire contents of the bottle.

If uncertain about quantity to add, add only half of the calculated amount of $K_2$DMcT solution required for neutralization. Shake contents, remove one gram of slurry, then measure pH. Keep adding $K_2$DMcT solution until pH is in the 7.2 to 7.5 range. Record final pH and total amount of 5% $K_2$DMcT solution added.

**The final step for this process required a drying step**: (*This step is required if the inhibitor is to be used in solvent borne formulations. If the product is to be used in water-borne formulations, omit this step.)*

14) Poured contents of beaker into large drying dish. This will take two to four days. Weigh a beaker, or preferably an evaporating dish. Remove air dried powder to beaker and record total mass. Place beaker and contents in vacuum oven at 40 - 50$^{o}$C and a vacuum of at least -28 in Hg. After a few hours, check weight. Check weight change after every few hours (or overnight) until weight change is less than 0.1% by weight of the product.

### 4.1.4.2 Adhesion Studies of Crosslink Primer Systems

A series of Crosslink inhibitor systems were tested for crosshatch and wet-tape adhesion according to their respective ASTM methods. Pass and fail was assigned to each inhibitor system depending on the requirements spelled out in the ASTM method. The Crosslink inhibitor underwent several modifications during the course of this laboratory study in order to improve their properties and to meet the minimum requirements of the adhesion tests.

#### 4.1.4.2.1 Crosshatch Adhesion Studies of Crosslink Primer

The testing of the Crosslink inhibitor was tested with and without inhibitors and coated over CCC or trivalent chromium pretreatment (TCP). Several different formulations of the Crosslink inhibitor were tested. A cross section of the Crosslink primer systems studied is shown in Tables 48-50. Modifications to the formulation were required to meet the ASTM test criteria. The crosslink primer systems studied were labeled as ESTCP U1 (30 wt% ZnDMcT); ESTCP FA1/FA3(22/ 25 wt% ZnDMcT) and ESTCP XL2 (7.5 wt % ZnDMcT). The latter formulation was required by the ESTCP review panel in order to minimize the number of variations in inhibitor concentrations that was studied. Both solvent-borne and water-borne formulations were prepared and tested using the various inhibitor systems. The inhibitor system was mixed into an epoxy based formulation and coated over CCC pretreatment on AA 2024-T3 substrate. In all Crosslink primer systems all formulations passed this test with a rating $\geq$ 4B.

**Table 48**: Cross-Hatch Adhesion Results (ESTCP U1)

| Panel ID | Dry Film Thickness | Coating | ASTM |
|---|---|---|---|
| UI-A1F-1 | 1.4 | Dual Spray SB (30%) ZnDMcT, New Inhibitor, New A Ball Milled, Fresh CCC | 5B |
| UI-A1A-3 | 0.8 | Dual Spray SB (30%) ZnDMcT, New Inhibitor, New A Ball Milled, Aged CCC | 5B |
| UI-A2F-1 | 1.1 | Dual Spray SB (30%) ZnDMcT, New Inhibitor, New A Not Ball Milled, Fresh CCC | 4B |
| UI-A3F-1 | 0.9 | Dual Spray SB (30%) ZnDMcT, New Inhibitor, New A Not Ball Milled, Fresh CCC | 4B |
| UI-B1F-2 | 0.6 | Blank SB, New A Ball Milled, Fresh CCC | 5B |
| UI-B3F-3 | 0.7 | Blank SB, Aged A Ball Milled, Fresh CCC | 5B |
| UI-B3A-3 | 0.6 | Blank SB Aged A Ball Milled, Aged CCC | 5B |

**Table 49**: Cross-Hatch Adhesion Results (ESTCP FA1)

| Panel ID | Dry Film Thickness | Coating | ASTM |
|---|---|---|---|
| 1-DS1-NC1 | 0.9 | Dual Spray SB (22%) ZnDMcT, Using 010208 Slurry, on 052709 CCC panel | 5B |
| FA1-DS2-NC3 | 0.6 | Dual Spray SB (22%) ZnDMcT, Using 080509AP Slurry, on 052709 CCC panel | 4B |
| FA1-DS3-NC3 | 0.8 | Dual Spray SB (22%) ZnDMcT, Using 083109 Slurry, on 052709 CCC panel | 5B |
| FA1-DM1-NC2 | 0.6 | Direct Mix (30%) Pigmentan, on 052709 CCC panel | 4B |
| FA1-DM2-NC3 | 1.2 | Direct Mix (30%) Using Corrlink 30A 050409, on 052709 CCC panel | 4B |

**Table 50**: Cross-Hatch Adhesion Results (ESTCP XL2)

| Panel ID | Dry Film Thickness | Coating | ASTM |
|---|---|---|---|
| L2-A-P9 | 1.4 | 7.5% Corrlink30A & 5% Pig E | 5B |
| XL2-A-P10 | 1.4 | 7.5% Corrlink30A & 5% Pig E | 5B |
| XL2-A-P11 | 1.4 | 7.5% Corrlink30A & 5% Pig E | 4B |
| XL2-DNC-P1 | 1.1 | Deft Non-Chrome Primer | 5B |
| XL2-DNC-P2 | 1.2 | Deft Non-Chrome Primer | 5B |
| XL2-DNC-P3 | 1.1 | Deft Non-Chrome Primer | 5B |
| XL2-DC-P10 | 1.0 | Deft Chrome Primer | 5B |
| XL2-DC-P11 | 1.0 | Deft Chrome Primer | 5B |
| XL2-DC-P12 | 0.9 | Deft Chrome Primer | 5B |
| XL2-A-T10 | 2.7 | 7.5% Corrlink30A & 5% Pig E | 4B |
| XL2-A-T11 | 2.6 | 7.5% Corrlink30A & 5% Pig E | 3B |
| XL2-A-T12 | 2.9 | 7.5% Corrlink30A & 5% Pig E | 3B |
| XL2-DNC-T1 | 2.7 | Deft Non-Chrome Primer | 4B |
| XL2-DNC-T2 | 2.6 | Deft Non-Chrome Primer | 4B |
| XL2-DNC-T3 | 2.5 | Deft Non-Chrome Primer | 4B |
| XL2-DC-T1 | 2.8 | Deft Chrome Primer | 5B |
| XL2-DC-T2 | 3.1 | Deft Chrome Primer | 5B |
| XL2-DC-T3 | 2.5 | Deft Chrome Primer | 5B |

#### 4.1.4.2.2 Wet Tape Adhesion Studies of Crosslink Primer

Wet-tape adhesion studies were performed on several Crosslink primer systems. Several of the primer systems studied are the following: ESTCP U1 (30 wt% ZnDMcT); ESTCP FA1/FA3 (22/ 25 wt% ZnDMcT) and ESTCP XL2 (7.5 wt % ZnDMcT). The wet-tape adhesion results for ESTCP U1 showed that are panels failed this test. These results were considered inconclusive and no trends could be determined that affected the adhesion performance.

Modifications were made to the Crosslink primer system. The new Crosslink primer system, ESTCP FA3 was designed to look at a maximum loading of Corrlink 30A at 25% alone or in various combinations with Pigmentan E. The results showed a dramatic improvement in the wet-tape adhesion of the modified Crosslink primer system. All formulations tested passed the minimum requirement of ≥ 4A (see Table 51). In addition, ESTCP XL2 (7.5 wt % ZnDMcT) also showed passing results for the wet-tape adhesion testing (see Table 52).

**Table 51**: Wet-Tape Adhesion Results (ESTCP FA3)

| Panel ID | Dry Film Thickness mils | Inhibitor | Rating / Pass-Fail | Observations |
|---|---|---|---|---|
| FA3-C3-A | 2.9 | Direct Mix (25%) Corrlink30A | 5A | None |
| FA3-C4-A | 2.8 | Direct Mix (25%) Corrlink30A | 5A | None |
| FA3-C6-A | 2.9 | Direct Mix (25%) Corrlink30A | 5A | None |
| FA3-G3-A | 2.8 | 50:50 Blend Corrlink30A/ Pigmentan E (6%/6%) | 5A | None |
| FA3-G4-A | 3.0 | 50:50 Blend Corrlink30A/ Pigmentan E (6%/6%) | 5A | None |
| FA3-G6-A | 2.7 | 50:50 Blend Corrlink30A/ Pigmentan E (6%/6%) | 5A | None |
| FA3-H3-A | 2.9 | 50:50 Blend Corrlink30A/ Pigmentan E (4%/4%) | 5A | None |
| FA3-H4-A | 2.7 | 50:50 Blend Corrlink30A/ Pigmentan E (4%/4%) | 5A | None |
| FA3-H6-A | 2.8 | 50:50 Blend Corrlink30A/ Pigmentan E (4%/4%) | 5A | None |
| FA3-J5-A | 3.0 | 50:50 Blend Corrlink30A/ Pigmentan E (8%/8%) | 5A | None |
| FA3-J6-A | 3.2 | 50:50 Blend Corrlink30A/ Pigmentan E (8%/8%) | 5A | None |

**Table 52:** Wet-tape Adhesion Results (ESTCP XL2)

| Panel ID | Dry Film Thickness mils | Inhibitor | Rating | Observations |
|---|---|---|---|---|
| XL2-A-P2-A | 1.2 | 7.5% Corrlink30A & 5% Pig E | 5A | Pass |
| XL2-A-P3-A | 1.2 | 7.5% Corrlink30A & 5% Pig E | 5A | Pass |
| XL2-A-P4-A | 1.5 | 7.5% Corrlink30A & 5% Pig E | 5A | Pass |
| XL2-A-T1-A | 3.0 | 7.5% Corrlink30A & 5% Pig E | 4A | Pass |
| XL2-A-T2-A | 2.7 | 7.5% Corrlink30A & 5% Pig E | 4A | Pass |
| XL2-A-T6-A | 2.9 | 7.5% Corrlink30A & 5% Pig E | 4A | Pass |
| XL2-DC-P13-A | 1.2 | Deft Chrome Primer | 5A | Pass |
| XL2-DC-P14-A | 1.2 | Deft Chrome Primer | 5A | Pass |
| XL2-DC-P15-A | 1.3 | Deft Chrome Primer | 5A | Pass |
| XL2-DC-T11-A | 2.3 | Deft Chrome Primer | 4A | Pass |
| XL2-DC-T12-A | 2.4 | Deft Chrome Primer | 4A | Pass |
| XL2-DC-T13-A | 2.5 | Deft Chrome Primer | 4A | Pass |
| XL2-DNC-P4-A | 1.1 | Deft Non-Chrome Primer | 5A | Pass |
| XL2-DNC-P5-A | 1.2 | Deft Non-Chrome Primer | 5A | Pass |
| XL2-DNC-P6-A | 1.2 | Deft Non-Chrome Primer | 5A | Pass |
| XL2-DNC-T10-A | 2.6 | Deft Non-Chrome Primer | 4A | Pass |
| XL2-DNC-T11-A | 2.8 | Deft Non-Chrome Primer | 4A | Pass |
| XL2-DNC-T12-A | 3.3 | Deft Non-Chrome Primer | 4A | Pass |

#### 4.1.4.3 Neutral Salt Spray Results of Crosslink Primer Systems

**The Crosslink corrosion inhibitor at different concentrations and coated onto various substrates using different pretreatment and topcoat combinations were tested by Crosslink in NSS chambers**.

The initial corrosion results (ASTM B117 neutral salt spray) from ESTCP U1 did not provide corrosion protection past 3000 hours on AA 2024-T3. The study was terminated after 2900 hours of salt fog exposure. These results verify the efficacy of using Corrlink 30A vs. a blank control. However, these also show that corrosion results needed improvement in performance in both dual-spray solvent-borne as well as in the water-borne direct mix formulation. Improvements in corrosion performance were seen with modifications of the Crosslink corrosion inhibitor concentration. Various combinations of Corrlink 30A and Pigmentan E (as 50/50 mixtures) were compared to a formulation with a 25% loading of Corrlink 30A. This had been the inhibitor level of prior formulations that had shown very good corrosion performance. Results from this round of testing showed that the various mixtures of inhibitors in the formulations gave equal performance to the formulation with 25% Corrlink 30A after 2500 hours.

Further studies looked at the compatibility of the ESTCP FA3 Crosslink inhibitor formulation with various pretreatments (CCC and TCP) with topcoat on AA 2024-T3. The best results after 2500 hours of exposure were obtained on CCC pretreated panels with a combination of 9% Corrlink 30A and 6% of Pigmentan E. These outperformed even the formulations with 25% Corrlink30A. The worst results were seen in the Deft non-chromate system on TCP, and this coating also performed poorly on CCC pretreatments.

The best performer in ESTCP FA4, the 9/6 formulation, was taken and the effect of various sources of the zinc salt was evaluated in ESTCP FA5. Three methods of incorporating the zinc salt inhibitor were used, 1) through a commercial product, Hybricor 204 (provided by Wayne Pigments Corp. Inc.), 2) the standard synthesis method (Corrlink 30A), and 3) through the Occidental process. Coatings were evaluated with and without topcoats. Results after 2500 hours in which all panels were pretreated with CCC, were the best performing system It was found that as a primer-only application, the three sources gave very similar results, and all outperformed the Deft non-chromate system. **With the topcoat application, the results were: Occidental process> Hybricor 204> Corrlink 30A> Deft non-chromate.**

The topcoated studies were continued in ESTCP U2, and results are reported in Table 39. In this set of results, it was found that the 9/6 formulation outperformed all other formulations, including chromate primer, in testing on CCC pretreated panels. On TCP, however, the 9/6 suffered from significant undercutting and did not compare well against the chromate control. The 7.5/5 formulation was not as good as the 9/6 formulation on either pretreatment. However, the current non-chromate control had the worst corrosion performance of all the coatings tested regardless of pretreatment used.

The Crosslink formulation (ESTCP XL1) tested on TCP, CCC and BAM-PPV. Both the 9/6 and 7.5/5 Corrlink 30A/Pigmentan E formulations were evaluated, along with a chromate control as well as a non-chromate control. The 7.5/5 formulation testing on BAM-PPV was terminated at 2168 hours, due to poor adhesion of the coating resulting in flaking. The rest of the panels were evaluated at 2500 and 3200 hours. In this

round of tests, the best results were obtained from the 7.5/5 formulation on CCC pretreatment, which outperformed even the chromate control after 2500 and 3200 hours. On TCP, however, the chromate control was better than the 7.5/5, especially after 3200 hours when significant blistering occurred on the latter. The 9/6 formulation was found to have suffered from blistering, even after only 2500 hours, which was different from what was seen in ESTCP U2 (Table 39). The Deft non-chromate coating had poor performance regardless of the pretreatment.

In ESTCP XL2, the corrosion performance of the 7.5/5 formulation was compared to the BoeAero formulation (containing 25% Corrlink 30A) as well as a similar formulation containing the same inhibitor but manufactured by Wayne Pigment Corp. Inc. Deft chromate and non-chromate coatings were again used as controls as well as the effects topcoats. This study was undertaken to evaluate the effect of a scaled-up process on the activity of the zinc inhibitor.

As a primer-only coating, the performance of the BoeAero formulation was similar after 2500 hours, whether the zinc salt was prepared by Crosslink or obtained from Wayne Pigments. The BoeAero formulation outperformed even the chromate control in this case. The 7.5/5 formulation without a topcoat was better than the chromate control for scribe appearance but suffered from blister formation. When a topcoat was applied, the 7.5/5 formulation was found to be the best performer. This showed that formulation improvements to make the primer more compatible with a topcoat were effective. The Crosslink-sourced inhibitor in the BoeAero formulation performed better than the one from Wayne Pigments, which suffered from undercutting.

The BoeAero formulations in the primer-only application performed so well that testing was extended to 8500 hours when significant failure was noted. After this length of time, it was found that the Wayne Pigment version of the inhibitor outperformed the Crosslink-sourced material in all 3 categories:

- scribe appearance,
- undercutting,
- and blister formation.

This indicated that scaling up of the zinc salt manufacturing process gave improved material quality from a corrosion inhibition standpoint.

In an alternative Crosslink formulation (ESTCP FA7), the $Zn(DMcT)_2$ inhibitor was incorporated into a proprietary 3K formulation obtained from a commercial coatings company. This was done to evaluate the ease of incorporation of the inhibitor into existing coatings formulations, and to determine if the corrosion performance would be unchanged from the previous 7.5/5 formulation. The commercial formulation did perform equal to the chromate control (2000 hours) as the primer-only application. This was both on CCC-pretreated panels for both AA 2024-T3 and AA 5182-T0. With a topcoat, performance was the same on AA 2024-T3, and the chromate control was slightly better on AA 5182-T0. Upon the extension of the test to 5000 hours the commercial 3K coating (primer-only) with Corrlink30A began to show some undercutting on AA 2024-T3 but not on AA 5182-T0. While some slight degradation was noted in the chromate controls after this time, this was attributed to imperfections in the coating process and not to actual corrosion occurring. When a topcoat was used, similar performance was seen in the

Corrlink 30A formulation and the chromate control on AA 2024-T3. Figures 149-158 show several examples of the Crosslink primer system on AA 2024-T3 and AA 5182-T0 in NSS exposure testing.

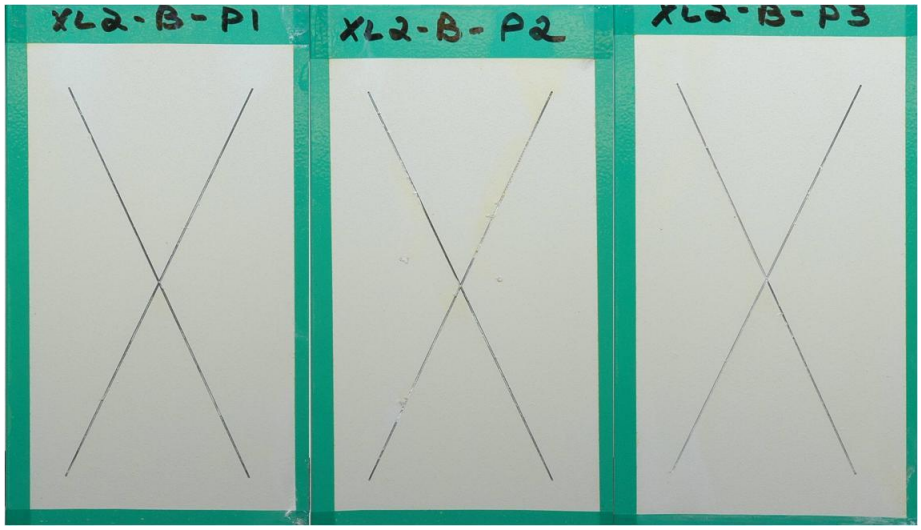



**Figure 149**: BoeAero (25% Corrlink 30A – lab scale, Primer only) on AA 2024-T3 after 8500 hours NSS

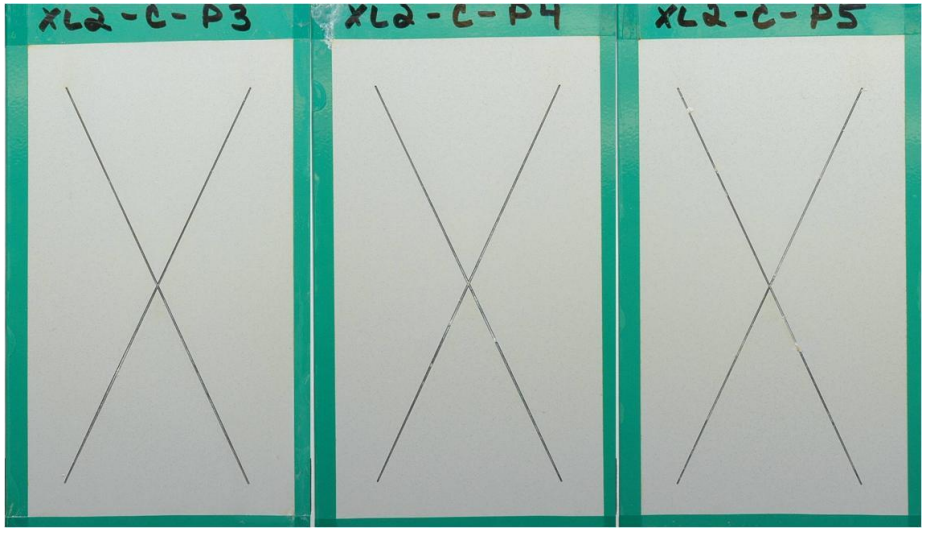



**Figure 150**: BoeAero (25% InhibiCor 1000 – pilot scale, Primer only) on AA 2024-T3 after 8500 hours NSS

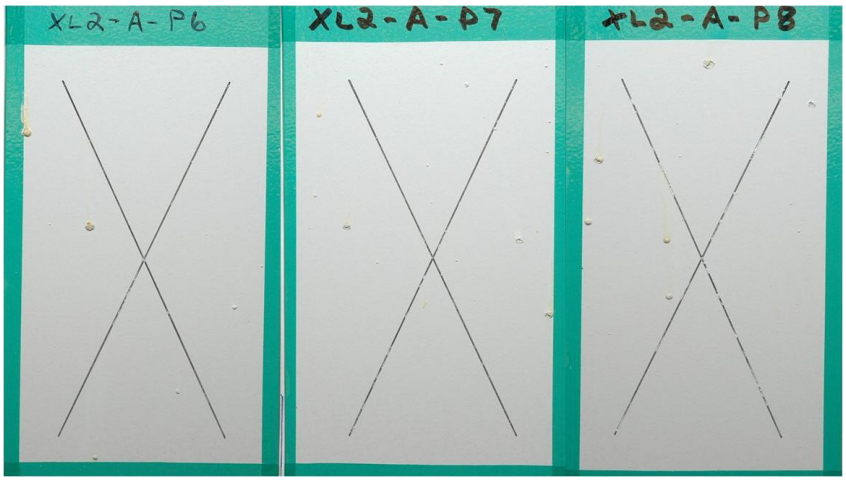



**Figure 151**: ESTCP 7.5/5 (BoeAero TC, Primer only)
on AA 2024-T3 after 2500 hours NSS

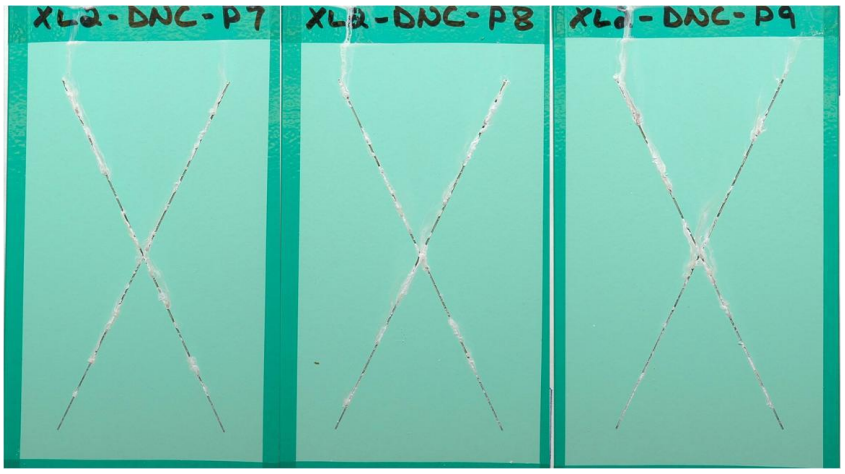



**Figure 152**: Deft Non-chromate on AA 2024-T3 after 2500 hours NSS

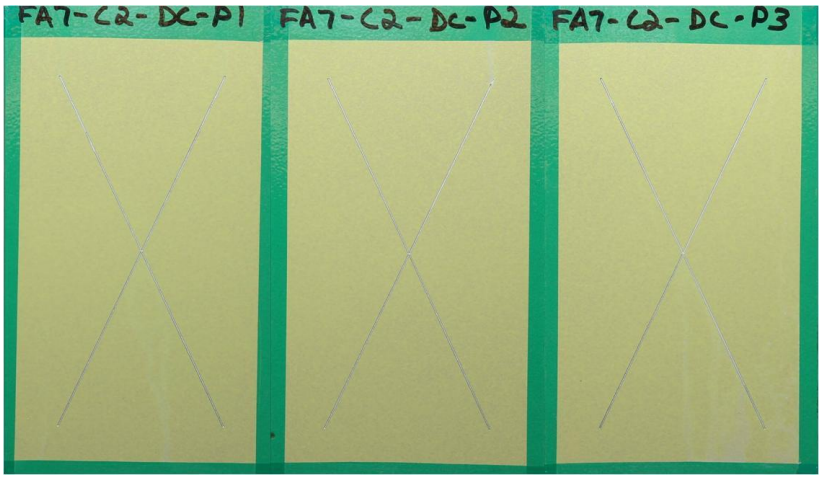



**Figure 153**: Deft Chromate Control on AA 2024-T3 after 3000 hours NSS

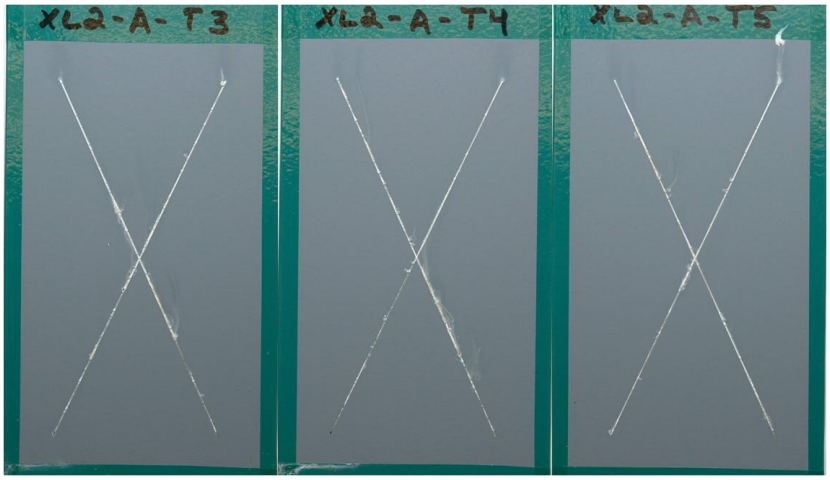



**Figure 154**: ESTCP 7.5/5, (BoeAero Topcoated)
on AA 2024-T3 after 2500 hours NSS

**Figure 155**: Deft Non-Chromate on AA 2024-T3 after 2500 hours NSS

**Figure 156**: Deft Chromate Control on AA 2024-T3 after 3000 hours NSS

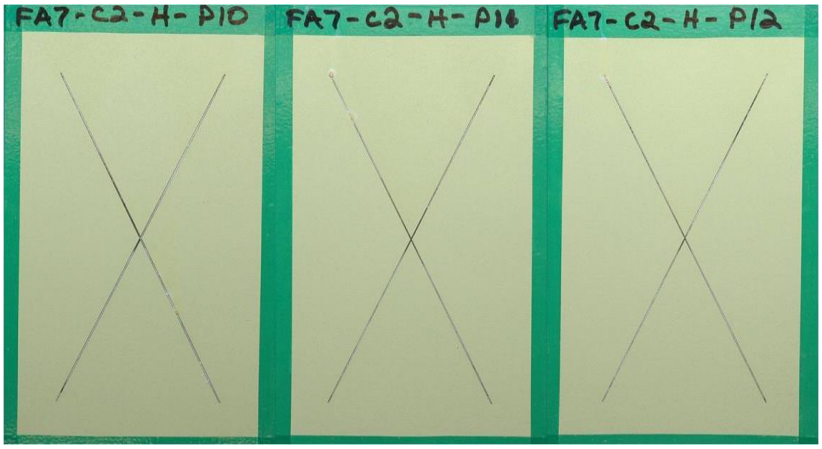



**Figure 157**: Commercial 3K Epoxy Resin, 25% InhibiCor 1000, Primer only on AA 2024-T3 after 5000 hours NSS

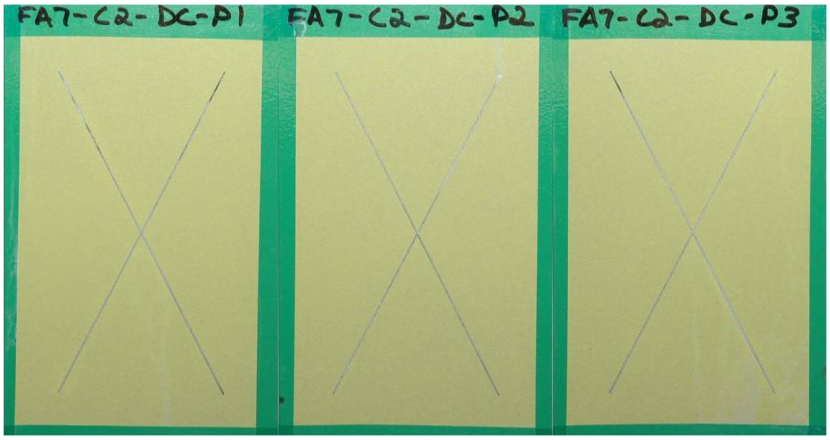



**Figure 158**: Deft Chromate Control on AA 2024-T3 after 5000 hours NSS

#### 4.1.4.4 Additional Tests for Crosslink Primer Systems

Several additional tests were performed on the Crosslink primer system. These tests include solvent resistance and impact flexibility. These two tests were required by the AF and Navy in order to determine the Crosslink primer robustness in full military coatings.

##### 4.1.4.4.1 Solvent Resistance Tests for Crosslink Primer Systems

The procedure used for solvent resistance by Crosslink researchers is described below. The procedure was in accordance with MIL-PRF-23377J - 4.4.1. The materials used for this study were a cotton terry cloth rag / Cheese cloth and a 24 oz ball peen hammer which was used for reproducibility. The solvent used for the rubs was MEK. The procedure for this test was as follows:

- Secure cheesecloth around end of ball peen hammer (several ply's thick) using rubber band to fasten,
- Soak cheesecloth with MEK solvent, rub the coating with the soaked cloth; (using the hammer weight for consistent pressure), for 50 passes (25 back and forth rubs). Rotate cheesecloth between panels and
- Examine coating for conformance to (MIL-PRF-23377H – 3.8.3.)

"Rubbing through to bare substrate constitutes failure of the primer coating to properly cure."

Table 53 shows the solvent resistance results for Crosslink primer system ESTCP U1 (30 wt% ZnDMcT). In this case, all panels and treatments failed to achieve the minimum of 50 rubs necessary. This indicated a major weakness in the formulation that was addressed with an improved formulation.

**Table 53**: Solvent Resistance Results for ESTCP U1

| Panel ID | Dry Film Thickness mils | Inhibitor | Pass/Fail | Number of Passes to Failure (50 passes = 25 back & forth) |
|---|---|---|---|---|
| UI-C1F-5 | 1.1 | Dual Spray SB (30%) ZnDMcT, Aged Inhibitor, New A Ball Milled, Fresh CCC | Fail | 28 passes |
| UI-C2F-4 | 1.1 | Dual Spray SB (30%) ZnDMcT, Aged Inhibitor, New A No Ball Milled, Fresh CCC | Fail | 21 passes |
| UI-C3F-2 | 0.9 | Dual Spray SB (30%) ZnDMcT, Aged Inhibitor, Aged A Ball Milled, Fresh CCC | Fail | 23 passes |
| UI-C3A-2 | 0.9 | Dual Spray SB (30%) ZnDMcT, Aged Inhibitor, Aged A Ball Milled, Aged CCC | Fail | 26 passes |
| UI-D4F-1 | 2.1 | Direct Mix WB, New Inhibitor, Water Dispersion, New CCC | Fail | 11 passes |
| UI-D4A-2 | 1.8 | Direct Mix WB, New Inhibitor, Water Dispersion, Aged CCC | Fail | 11 passes |

The modification of the Crosslink primer systems (ESTCP FA1/FA3 (22/25 wt% ZnDMcT) and ESTCP XL2 (7.5 wt % ZnDMcT)) have passed the solvent resistance tests (see Tables 54 and 55). Both tables show the improvement in properties with the incorporation of Pigmentan E. The incorporation of the Pigmentan E and lower Crosslink inhibitor (7.5 wt %) resulted in all formulations passing this test. This included the Corrlink-containing formulations with and without a topcoat. The Corrlink-containing formulations, despite being at the 7.5/5 mark, pass unequivocally, enduring more than 100 passes of the MEK rub. In these instances, the pretreatment of the panels was the CCC. The improved performance was also attributed to improvements in the formulation process.

**Table 54**: Solvent Resistance Results for ESTCP FA1/FA3

| Panel ID | Dry Film Thickness mils | Inhibitor | Pass/Fail | Number of Passes to Failure (50 passes = 25 back & forth) |
|---|---|---|---|---|
| FA1-DS1-NC1 | 0.9 | Dual Spray SB (22%) ZnDMcT, Using 010208 Slurry, on 052709 CCC panel | Pass | 59 passes |
| FA1-DS2-NC3 | 0.6 | Dual Spray SB (22%) ZnDMcT, Using 080509AP Slurry, on 052709 CCC panel | Pass | 75 passes |
| FA1-DS3-NC3 | 0.8 | Dual Spray SB (22%) ZnDMcT, Using 083109 Slurry, on 052709 CCC panel | Pass | 65 passes |
| FA1-DM1-NC2 | 0.6 | Direct Mix (25%) Pigmentan, on 052709 CCC panel | Pass | >100 passes |
| FA1-DM2-NC3 | 1.2 | Direct Mix (25%) Using Corrlink 30A 050409, on 052709 CCC panel | Fail | 19 passes |

**Table 55**: Solvent Resistance Results for ESTCP XL2

| Panel ID | Dry Film Thickness mils | Inhibitor | Pass/Fail | Number of Passes to Failure (50 passes= 25 back & forth) |
|---|---|---|---|---|
| XL2-A-P9 | 1.4 | 7.5% Corrlink30A & 5% Pig E | Pass | >100 rubs |
| XL2-A-P10 | 1.4 | 7.5% Corrlink30A & 5% Pig E | Pass | >100 rubs |
| XL2-A-P11 | 1.4 | 7.5% Corrlink30A & 5% Pig E | Pass | >100 rubs |
| XL2-DNC-P1 | 1.1 | Deft Non-chrome Primer | Pass | >100 rubs |
| XL2-DNC-P2 | 1.2 | Deft Non-chrome Primer | Pass | >100 rubs |
| XL2-DNC-P3 | 1.1 | Deft Non-chrome Primer | Pass | >100 rubs |
| XL2-A-T10 | 2.7 | 7.5% Corrlink30A & 5% Pig E | Pass | >100 rubs |
| XL2-A-T11 | 2.6 | 7.5% Corrlink30A & 5% Pig E | Pass | >100 rubs |
| XL2-A-T12 | 2.9 | 7.5% Corrlink30A & 5% Pig E | Pass | >100 rubs |
| XL2-DNC-T1 | 2.7 | Deft Non-chrome Primer | Pass | >100 rubs |
| XL2-DNC-T2 | 2.6 | Deft Non-chrome Primer | Pass | >100 rubs |
| XL2-DNC-T3 | 2.5 | Deft Non-chrome Primer | Pass | >100 rubs |

#### 4.1.4.4.2 GE Impact Flexibility Tests for Crosslink Primer Systems

The only Crosslink primer system tested for GE impact flexibility was the 7.5% Corrlink 30A/5%Pig E and this primer did pass this test. The procedure for this test is described below (see Table 56 for the rating and Table 57 for results from this test).

Procedure:

- The film thickness of anodized panels coated with resin / corrosion inhibitors system were measured and zero the instrument on the back of the panel where no coating is present. Flip the panel over and take measurements at four different places on the panel and then take the average of the measurements.

- Cut 6” x 3” panel down to 2 – 3” x 3” panels ( Making sure both sides are labeled with panel ID numbers )
- Place the reverse impact tester on the rubber mat on the floor and level the instrument.
- Place the panel (coating side down) on the stage and make sure that the impactor will land completely on the panel.
- Record the side of the impactor in use (A or B).
- Raise the impactor to specified height (34.5“) and let it drop.
- Remove the panel and examine it under the Leica (StereoZoom 5) microscope at 10× the magnification to determine if the coating cracked upon the impact.
- Record the % elongation that corresponds to that impression and determine if the panel passed or failed.

**Table 56**: Rating System for Evaluation of Impact-Flexibility Results

| **G.E. Impact-Flexibility Table** | | | | | |
|---|---|---|---|---|---|
| **Spherical Segment** | **End** | **Base Diameter** | **Segment Radius** | **Segment Elevation** | **% Area Increase** |
| 1 | A | 0.375 | 0.194 | 0.146 | 60 |
| 2 | A | 0.375 | 0.208 | 0.119 | 40 |
| 3 | A | 0.375 | 0.252 | 0.084 | 20 |
| 4 | A | 0.375 | 0.326 | 0.059 | 10 |
| 5 | B | 0.375 | 0.44 | 0.042 | 5 |
| 6 | B | 0.375 | 0.676 | 0.027 | 2 |
| 7 | B | 0.375 | 0.947 | 0.019 | 1 |
| 8 | B | 0.375 | 1.332 | 0.013 | 0.5 |
| *******Below 10% is failing.** | | | | | |

**Table 57**: GE Impact Flexibility Test Results

| XL1-ESTCP | | | | | |
|---|---|---|---|---|---|
| **G.E. Impact-Flexibility Results ( Impact testing performed 10/1/10)** | | | | | |
| **Panel ID** | **Dry Film Thickness mils** | **Inhibitor** | **% elongation** | **Pass/Fail** | **Observations** |
| An2-A1 | 0.6 | 7.5% Corrlink30A & 5% Pig E | 10% | P | None |
| An2-A2 | 0.6 | 7.5% Corrlink30A & 5% Pig E | 10% | P | None |
| Inch pounds of drop is determined by multiplying height in inches by the pound weight. ( 34.5" x 3.6 lbs = 124.2 ) | | | | | |
| Used the Leica ( StereoZoom 5 ) Microscope (×10 magnification) to evaluate impact results | | | | | |

#### 4.1.4.3 Conclusions of Laboratory Testing Performed by Crosslink

The Crosslink primer was modified to meet the military requirements for a non-Cr(VI) primer coating. The results of the two-year Crosslink laboratory studies are presented in bullet form.

- Through various changes in the formulation of the 3K system, Crosslink successfully improved the performance of the primer coatings with respect to the method of application and mechanical properties.
- The solvent-borne 3K system was successfully transitioned from requiring a 2-gun application to one having a direct mix formulation requiring a single gun.
- The reduction of the $Zn(DMcT)_2$ content from 25% to improved the wet adhesion properties of the primer as well as led to improved solvent resistance.
- The addition of Pigmentan E, further improved the wet adhesion and solvent resistance properties of the coating and a blend of 7.5%/5% Corrlink30A:Pigmentan E was finally chosen as the best ratio for use in the internal Crosslink primer formulation.
- This formulation passed all mechanical tests including the water resistance test, with and without a topcoat.
- For corrosion inhibition on aluminum 2024-T3, the best results were obtained with the highest (25%) Corrlink 30A loading in the formulations, using CCC pretreated panels, with corrosion inhibition equaling that from chromate controls up to 8500 hours.
- When a topcoat was applied, a formulation containing 7.5/5 (%) of Corrlink 30A and Pigmentan E provided the best results for corrosion

control up to 2500 hours, with results equal to or better than chromate based coatings.

- The $Zn(DMcT)_2$ salt, known as Corrlink 30A internally, was shown to be reproducibly made at the laboratory scale and offered excellent corrosion protection on aluminum and was scaled-up to 200 lbs. in pilot production through the formation of a business venture between Crosslink and WPC Technologies, Inc.
- The scaled up material, known as InhibiCor 1000, was tested and showed properties similar to Corrlink 30A for corrosion inhibition and mechanical properties in coatings formulations.

## 5.0 COST ASSESSMENT

Once the Crosslink primer is approved for use by military organizations, the cost to implement within the DOD should be minimal. This is because the Crosslink primer can be applied via HVLP, the primary system utilized by AF, Navy and Army maintenance operations. The need for extensive PPE, hazardous waste removal, employee monitoring, and other expenses associated with Cr(VI) primers does not exist with the Crosslink primer coating. Packaging and availability of the final product will need to be determined by an appropriate vendor (Hentzen) who has scaled-up this technology for industrial production.

As there does not seem to be costs associated with equipment change for application of the Crosslink primer, the change in cost would be due to change in application time, savings from hazardous waste disposal costs, and savings in depainting costs because Crosslink primer is Cr(VI)-free. The costs for facility capital are minor since most depots and maintenance sites use commercial-off-the shelf (COTS) HVLP spray equipment. These sites all have spray booths and this is where the majority of the application of Crosslink primer coating will occur. There should be no costs associated for equipment changes or operations/maintenance issues other than the present requirements associated with Cr(VI) primers. There is also no equipment replacement for applying the Crosslink primer solution onto various substrates.

The ESOH regulations do not apply to the Crosslink primer due to its non-hazardous, non-toxic properties and any costs associated with ESOH compliance are avoided. The application of the Crosslink primer will require only PPE during painting operations. The following table 58 provides the cost analysis of the Crosslink primer to commercial Cr(VI) primer coatings.

**Table 58**. Cost Comparison of Crosslink Primer to Cr(VI) Primer

| **Primer System** | **Price($)/gallon** | **Coverage (sq. ft.)** | **$ per sq. ft.** |
|---|---|---|---|
| Cr(VI) PRIMER | 32.00 | 937 | 0.03 |
| CROSSLINK PRIMER | 85-120 | 937 | 0.09-0.13 |

As can be seen from Table 58 the Crosslink primer while slightly more expensive is still competitive with the Cr(VI) primer cost. If implementation of the Crosslink primer after successful field-test demonstration occurs, the initial costs to the military will be off-set by savings in eliminating hazardous disposal costs.

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# APPENDIX A: POINTS OF CONTACT

| POINT OF CONTACT Name | ORGANIZATION Name Address | Phone/Fax/email | Role in Project |
|---|---|---|---|
| Peter Zarras | NAWCWD<br>(Code 4L4200D)<br>19090 N. Knox Road (Stop 6303)<br>China Lake, CA 93555-6106 | 760-939-1396<br>769-939-1617<br>Peter.zarras@navy.mil | Manager overall project coatings |
| Cindy Webber | NAWCWD<br>(Code 4L4200D)<br>19090 N. Knox Road (Stop 6303)<br>China Lake, CA 93555-6106 | (P) 760-939-2060<br>(F) 769-939-1617<br>cynthia.webber@navy.mil | Coating processing |
| Gusphyl (Gus) Justin | WPC Technologies, Inc.<br>300 South Barclay Street<br>Milwaukee, WI 53204 | (P) 414 755-8725<br>(F) 414-225-2410<br>gjustin@wpoctech.com | Coating and testing |
| Amy Fowler | NAWCAD, Code 4.3.4.2<br>48066 Shaw Road<br>Bldg 2188<br>Patuxent River, MD 20670-1906 | (P) 301-342-0986<br>(F) 301-342-7566<br>Amy.Fowler@navy.mil | Coating management |
| Christopher E. Miller | Army Research Laboratory<br>Coatings and Corrosion<br>Building 4600<br>ARSRD-ARL-WM-SG<br>Aberdeen Proving Ground, M21005-5069 | (P) 410-306-0849<br>(F) 410-306-0613<br>cemiller@arl.army.mil | Coating management |
| Diane Buhrmaster | Coatings Research Scientist<br>University of Dayton Research Institute<br>300 College Park<br>Dayton, OH 45469-0054 | (P) 937-656-9549<br>(F) 937-255-0954<br>Diane.Buhrmaster@WPAFB.AF.MIL | Coating management |