



# Processing, Adhesion and Corrosion-inhibiting Properties of Poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene], (MEH-PPV) on Aerospace Aluminum Alloys

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**Abstract:** Researchers at the Naval Air Warfare Center Weapons Division (NAWCWD) and Wright-Patterson Air Force Base (WPAFB) investigated poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene], (MEH-PPV) for its potential corrosion-inhibition properties on aerospace aluminum alloy AA2024-T3. Solution processing of the polymer, as well as adhesion testing and accelerated weathering tests were performed on MEH-PPV full military aerospace coatings. Wet and dry tape adhesion testing, as well as pencil hardness, impact flexibility and pneumatic adhesion tensile test instrument (PATTI) testing were used to demonstrate the adhesion performance of MEH-PPV on aluminum substrates. The results showed that MEH-PPV had acceptable adhesion characteristics when compared to hexavalent chromium (Cr(VI)) based coatings in all of these tests. Accelerated weathering analysis was performed on MEH-PPV coatings to determine their corrosion protection and weathering resistance capabilities. These tests included neutral salt spray (NSS) exposure and xenon-arc lamp testing. The results showed that while MEH-PPV does not exhibit significant color change after 500 hours of xenon arc lamp exposure, the polymer has poor corrosion protection performance under aggressive salt environments.

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## 1. INTRODUCTION

The United States military relies on multi-component protective coating systems to maintain operational readiness of military aircraft. Current high-performance aerospace coating systems consist of three layers, a pretreatment, primer and topcoat. Coatings for the military center on the use of hexavalent chromium (Cr(VI)) in both the pretreatment and primer layers. The current aerospace coating has been developed over many years to meet the strenuous challenges of corrosion, adhesion and weathering encountered by military platforms [1, 2].

Chromate conversion coatings (CCC's) and Cr(VI) primers are effective at inhibiting corrosion because they can provide

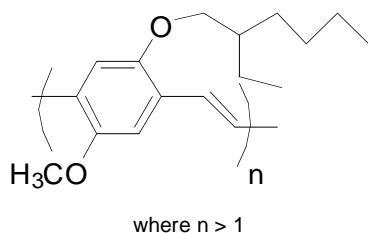
corrosion-inhibition of metals and alloys via a "self-healing" mechanism. The CCCs and Cr(VI) primers acts as a reservoir of mobile Cr(VI) that is capable of migrating to defects and inhibiting further corrosion by forming passivating layers on the metal surface [3-6]. However, Cr(VI) is a known carcinogen and toxin to humans and the environment [7].

Over the past 25 years, published evidence that electro active polymers (EAPs), such as polyaniline (PANI), can inhibit corrosion has come from the pioneering work of Mengoli [8], DeBerry [9] and MacDiarmid [10]. Mengoli showed that EAP coatings deposited onto iron anodes by electro polymerization of aniline resulted in an adherent and corrosion inhibiting film. Further work by DeBerry showed that PANI electrochemically deposited onto stainless steel in sulfuric acid solution changed the corrosion behavior of the stainless steel substrate. This work demonstrated that the PANI film provided anodic protection, thus, maintaining a

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native passive film on the steel. There are numerous studies [11-15] and recent reviews [16, 17] documenting the corrosion-inhibiting properties of EAPs deposited onto metal alloys. An EAP derivative of poly(*p*-phenylene vinylene), specifically poly(2,5-bis(*N*-methyl-*N*-hexylamino)phenylene vinylene)(BAM-PPV), that was synthesized and coated onto an aluminum alloy (AA2024-T3), passed laboratory corrosion testing and survived a one year field study. These studies confirmed that BAM-PPV provided corrosion protection for AA2024-T3 alloy via a passivation mechanism and can be used as a pretreatment coating replacement for CCC's [18-20].

Since BAM-PPV showed corrosion-inhibition on aerospace aluminum alloys, we chose to investigate poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene], MEH-PPV (Figure 1), which has a similar structural backbone, essentially the oxygen analog to BAM-PPV, as a CCC replacement. MEH-PPV has been investigated for such applications as polymer light emitting diodes [21], solar cells [22], polymer lasers [23] and polymer field-effect transistors [24], but the potential application of MEH-PPV as a corrosion-inhibition coating has not been reported.



**Figure 1:** Poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene](MEH-PPV).

The Naval Air Warfare Center Weapons Division (NAWCWD) and Wright Patterson Air Force Base (WPAFB) tested MEH-PPV as a potential corrosion-inhibiting pretreatment coating on AA2024-T3 aerospace alloy. The only previously reported testing of MEH-PPV as a corrosion inhibiting pretreatment was a preliminary study performed by the authors, which showed that MEH-PPV coated onto AA2024-T3 can inhibit corrosion in neutral salt spray (NSS) exposure testing for 336 hours [18]. It is a military requirement for CCC replacements that the alternative survive 336 hours NSS without any evidence of corrosion, blistering or delamination from the substrate. In these specific tests the coated coupons are not scribed.

These initial studies were followed with further laboratory testing, reported here, which conform to Air Force military requirements for alternative pretreatment coatings to be used as replacements for CCCs in full military aerospace coatings (pretreatment, epoxy primer and polyurethane APC (Advanced Performance Coating, aka Extended Life Topcoat, now listed in MIL-PRF-85285 as Type IV top coat). The goals of this laboratory study were to ascertain the robustness of an MEH-PPV pretreatment coating incorporated into full, Cr(VI)-

free aerospace coatings compared to a Cr(VI)-based aerospace coating.

## 2. EXPERIMENTAL

### 2.1. Materials

The monomer, 1,4-Bis(chloromethyl)-2-(2-ethylhexyloxy)-5-methoxybenzene was prepared according to a previously reported procedure developed by the authors [25]. The polymer, poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene], MEH-PPV was also prepared via previously reported methods [26-28]. 1-Chloro-4-(trifluoromethyl) benzene (Oxsol 100), acetone, methanol, and Alconox were purchased from Sigma-Aldrich Chemical Company and used as received. Aluminum alloy AA2024-T3 and CCC coupons were purchased from Q-Lab Corporation. Aluminum alloy coupons were purchased pre-coated with CCC. The coverage of the CCC was 100mg/ft<sup>2</sup>. MEH-PPV was coated onto aluminum substrates as described below.

### 2.2. Solution Processing of MEH-PPV Using Oxsol 100

MEH-PPV powder was dissolved in the VOC-exempt solvent Oxsol 100. Complete dissolution of the MEH-PPV to produce 1% (w/w) solutions required more than 4 hours, at elevated temperature with agitation (100-150°C, stir plate set to 300 rpm).

### 2.3. Application of Aerospace Coatings to Aluminum Coupons

MEH-PPV solutions were removed from the stir plate after 24 hours and applied to AA2024-T3 substrates after surface cleaning of the aluminum alloy using acetone, methanol, and 5% (w/v) Alconox in DI water followed by DI water rinse and air drying. High volume low pressure (HVLP) spray was used to apply the MEH-PPV solution, primers and MIL-PRF-85285 Type IV topcoat, respectively. General HVLP settings for the application of MEH-PPV solutions are given in Table 1. Six to eight cross coats were applied to the coupons, which resulted in film thicknesses of between 1-2µm. A thickness of 1-2µm was used because previous studies of the structurally similar polymer BAM-PPV showed that a thickness of at least 1µm was necessary to provide adequate corrosion protection [29]. The thickness of the MEH-PPV pretreatment layer was calculated to be between 1-2µm, as determined by measuring the mass difference before and after the coupons were coated, and assuming that the density of MEH-PPV matches that of BAM-PPV (1.0 g/cm<sup>3</sup>), which has been measured previously [16]. It was found that the coating could be applied in multiple cross-coats on near-vertical surfaces with a 5 minute flash-off period after every 2-3 cross-coats. Set-to-touch time for the MEH-PPV coating was less than 30 minutes. Primers were mixed according to the manufacturer's instructions and the coatings were applied using a single cross coat with the same HVLP spray parameters listed in Table 1. After 4 hours, substrates were top coated with MIL-

PRF-85285 Type IV. This topcoat was mixed according to the manufacturer's instructions and applied using the same settings. Samples were left to cure at room temperature and ambient relative humidity (approximately 75 °F and 50% RH) for 14 days prior to testing. A description of the primers, topcoat and dry-film thickness according to military specification, MIL-PRF-23377K, Type I, Class C and N is found in Table 2 [30].

**Table 1: HVLP Spray Application Parameters for MEH-PPV Solution**

Line PSI	30 psi
Fluid Setting	1.5 mL
Hose inner diameter	3/8"
Hose length	30'
HVLP Gun	GTI
Needle Size	#413
Cap Size	#100
Cap PSI	<10
Application Notes:	Material applied with a 5 min flash-off period between each 2–3 cross-coats

## 2.4. Qualitative Adhesion Studies

### 2.4.1. Crosshatch Adhesion

Crosshatch adhesion testing was performed to determine the adhesion between the substrate, pretreatment, primer and

topcoat interfaces on AA2024-T3 substrates. ASTM D 3359: Standard Test Methods for Measuring Adhesion by Tape Test was used for this analysis [31]. All coated substrates were tested with a 2-millimeter spacing crosshatch blade and there were three replicates for each coating system. The ratings categories are summarized in Table 3.

### 2.4.2. Wet-Tape Adhesion

The wet-tape adhesion test is specified in MIL-PRF-23377 and MIL-PRF-85285, and is designed to measure inter-coat adhesion of an organic coating [29, 31]. The organic coating was immersed in water for 24 hours and the wet-tape adhesion test was performed on three replicates for each coating system. Federal Test Method Standard (FTMS) 141D: Paint, Varnish, Lacquer and Related Materials: Methods of Inspection, Sampling, and Testing, Method 6301, Adhesion (Wet) Tape Test was used for this test and the ratings system is summarized in Table 4.

## 2.5. Quantitative Adhesion Studies

### 2.5.1. Pull-Off Adhesion

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. ASTM D 4541: Standard Test Method for Pull-Off Strength of Coatings Using Portable Adhesion Testers was used to perform this analysis [32]. There were three replicates for each coating system and

**Table 2: Air Force Primers and Topcoat Used for MEH-PPV Coated Coupons in Laboratory Studies**

Coating	Military Specification	Dry-film Thickness (Microns)	Description
Primer (control)	MIL-PRF-23377, Type I, Class C	15-23	two-component, epoxy polyamide primer containing SrCrO <sub>4</sub> inhibitors
Primer	MIL-PRF-23377, Type I, Class N	15-23	non-Cr(VI) based corrosion-inhibitors solvent-borne, high solids epoxy primer
Topcoat	MIL-PRF-85285 Type IV	43-58	VOC-compliant, chemically cured fluoropolyurethane topcoat

**Table 3: ASTM D 3359 Method B, Crosshatch Adhesion Rating Scale**

Rating Scale	Percent (%) Area Removed	Description
5B	0%	the edges of the square are completely smooth none of the squares of the lattice are detached
4B	< 5%	small flakes of the coating are detached at intersections less than 5% of the area is affected
3B	5-15%	small flakes of the coating are detached along edges and at the intersections of cuts
2B	15-35%	the coating has flaked along the edges and on parts of the squares
1B	35-65%	the coating has flaked along the edges of the cuts in large ribbons and whole squares have detached
0B	>65%	severe flaking and detachment across entire square

Table 5 lists the descriptions of various failure modes which were used as a guide for evaluating the coated coupon.

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

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

## 2.6. Pencil Hardness

Pencil hardness testing, during which pencils of increasing hardness are scribed on the surface until damage is observed, was performed on the coatings. This test was performed according to the Standard Test Method for Film Hardness by Pencil Test, ASTM D 3363 [33]. There were three replicates for each coating system, and the rating system from ASTM D 3363 that was used to evaluate the coatings is shown in Figure 2.

## 2.7. Impact Flexibility Testing

Impact flexibility was determined using the GE Model 172 reverse impact tester. As specified by MIL-PRF-85285, ASTM D 6905: Standard Test Method for Impact Flexibility of Organic Coatings was used for this analysis [34]. All samples were tested in triplicate.

## 2.8. Accelerated Weathering Tests

### 2.8.1. Xenon Arc Accelerated Weathering Test

Accelerated weathering of organic coatings by exposure to xenon arc light provides information about the degradation of the coating system by measuring the color of the sample before and after exposure. ASTM G 155: Standard Practice for Operating Xenon Arc Light Apparatus for Exposure of Non-Metallic Materials was used to perform this test [35]. To receive a “pass” rating in this test, a sample must have a color change value ( $\Delta E$ ) <1.

### 2.8.2. Neutral Salt Spray Exposure Testing

Neutral salt spray (NSS) exposure testing was performed to evaluate the ability of the coating systems to withstand a 5% (w/v) sodium chloride solution, pH-adjusted to a range of 6.5 – 7.2. ASTM B 117: Standard Practice for Operating Salt Spray (Fog) Apparatus was used for this analysis [36]. All samples subjected to NSS exposure were photographed before and after the test to document the coating performance and 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: Performance Specification, Primer Coatings: Epoxy, High Solids [30]. The rating system for aerospace coatings exposed to neutral salt spray is given in Table 6 and is derived from ASTM methods. The rating numbers are referenced in this order: 1<sup>st</sup> number = Scribe appearance, 2<sup>nd</sup> number = Undercutting and 3<sup>rd</sup> number = Blistering. After the

**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*
P/Pretreat	Primer on the stub and pretreatment on the panel	Primer–Pretreatment Adhesion
Pretreat/ Pretreat	Pretreatment on the stub and on the panel	Pretreatment–Pretreatment Cohesion

\*The epoxy noted in T/E and P/E failure modes is the epoxy that is used to attach the sample under test to the instrument. This epoxy is NOT part of the coating system.



**Figure 2:** ASTM D 3363 Pencil Hardness Rating System.

**Table 6: Scribe Appearance, Undercutting and Blistering Rating System**

Scribe Rating	Evaluation	Undercutting Rating	Evaluation	Blister Rating	Evaluation
0	Bright and Clean	0	No lifting of coating	0	None
1	Staining no corrosion build-up	1	Lifting or loss of adhesion up to 2 mm	1	Very small
2	Minor corrosion build-up	2	Lifting or loss of adhesion up to 3 mm	2	Small
3	Moderate corrosion build-up	3	Lifting or loss of adhesion up to 6 mm	3	Medium
4	Major corrosion build-up	4	Lifting or loss of adhesion up to 13 mm	4	Large
5	Severe corrosion build-up	5	Lifting or loss of adhesion > 13 mm	5	Delamination

0-5 ratings are recorded in each category, the sample is given an overall rating of “acceptable”, “low”, or “poor”.

### 3. RESULTS AND DISCUSSION

The following Table 7 summarizes the results from the adhesion (qualitative and quantitative), pencil hardness, impact flexibility, xenon arc and neutral salt spray (NSS) exposure laboratory testing for aerospace coatings based on the MEH-PPV pretreatment and the Cr(VI) control systems.

#### 3.1. Adhesion Testing Results

##### 3.1.1. Crosshatch Adhesion Test Results

The adhesion testing results documented in Table 7 show that MEH-PPV pretreatment coating incorporated into a full military aerospace system performs as well as, or better than, the Cr(VI) control in both dry and wet tape tests. The dry crosshatch adhesion test of MEH-PPV coated substrates showed no loss of the coating *via* visual inspection. The Cr(VI) based control coating showed some flaking at the intersections. No part of either coating was removed during the wet-tape adhesion test.

##### 3.1.2. PATTI Adhesion Test Results

The qualitatively determined adhesion strength of MEH-PPV was verified quantitatively with PATTI analysis. The pull-off

strength of the MEH-PPV coating was  $1878 \pm 100$ psi, which is more than twice the strength measured for the Cr(VI)-based control system. The MEH-PPV samples exhibited both a cohesive and an adhesive failure mode. Both of the failures involved the pretreatment layer, which is discouraging. However, the overall strength is high enough that the MEH-PPV system warranted further testing.

##### 3.1.3. Pencil Hardness and Impact Flexibility Testing Results

The MEH-PPV coating system performed equivalently to the Cr(VI) control in both pencil hardness and impact flexibility tests. The pencil hardness test is more applicable to top coatings, so it is not surprising that the samples performed equivalently. The impact hardness test can be influenced by the composition of the pretreatment layer. The results of the impact hardness test in this study show that the MEH-PPV organic coating system performed equivalently to the inorganic CCC coating system.

#### 3.2. Accelerated Weathering Test Results

##### 3.2.1. Xenon Arc Accelerated Weathering Test Results

Perceived color change in a coating system is important for marketability, and a xenon arc lamp exposure test is used to mimic extended exposure to sunlight, which causes color change in real world systems. In previous testing, AFRL has

**Table 7: Results from Laboratory Testing of MEH-PPV Coatings vs. Control**

Test Method	Aluminum Alloy (AA) Substrate	Cr(VI) Control Coating System	MEH-PPV Coating System
Crosshatch adhesion test	AA2024-T3	4B (Pass) (<5 %)	5B (Pass) (0 %)
Wet tape adhesion test	AA2024-T3	5A (Pass)	5A (Pass)
PATTI adhesion test	AA2024-T3	$792 \pm 100$ psi (P/P)	$1878 \pm 100$ psi (Pretreat/Pretreat)/(P/Pretreat)
Pencil hardness test	AA2024-T3	HB	HB
Impact flexibility test	AA2024-T3	10	10
Xenon arc test	AA2024-T3	0.6 (Pass)	0.6 (Pass)
NSS exposure test	AA2024-T3	2,0,0 (Acceptable)	3,4,0 (Poor)

\*Note: The layers in the chromate coating system and MEH-PPV coating system stack-ups are different colors, and are thus distinguishable visually.

observed that topcoat weathering behavior is directly related to the chemical composition of the primer underneath, and have also confirmed interactions between a primer and the topcoat at the molecular level [37]. Weathering phenomena were evaluated for both standard Cr(VI) and MEH-PPV coating systems to evaluate if a trend could be identified for tinted organic pretreatments as well. It is reasonable to expect that some discoloration may occur when using a conjugated organic pretreatment because of its high absorptivity in the UV-visible spectrum. However, we did not see significant discoloration. CIELAB color space was used for this testing and both Cr(VI) controls and MEH-PPV coated substrates were exposed to the xenon arc lamp for 500 hours. Both systems passed with  $\Delta E$  values of 0.6.

### 3.2.2. Neutral Salt Spray Test Results

NSS studies of the MEH-PPV coatings showed that in corrosive environments, despite the strong adhesion and good performance of structurally similar BAM-PPV coatings [38], the MEH-PPV coatings do not provide adequate corrosion protection for AA2024-T3 substrates. We determined that the MEH-PPV coating was responsible for the failure, because in analogous fully non-chromium coatings, the structurally similar BAM-PPV does provide adequate corrosion protection. Coatings that use a CCC as a pretreatment in conjunction with non-chromium primers also provide adequate corrosion protection, which indicates that the use of non-chromium primers does not cause coating failure, thus supporting the determination that MEH-PPV is the failure point [29]. The performance metric for the continued testing of a new coating system that is required by the United States Air Force is 2000 hours of exposure to a NSS with no evidence of corrosion. Figure 3 shows photographs of a representative MEH-PPV sample and a representative Cr(VI) control sample after NSS exposure. The image shows that extensive corrosion and undercutting

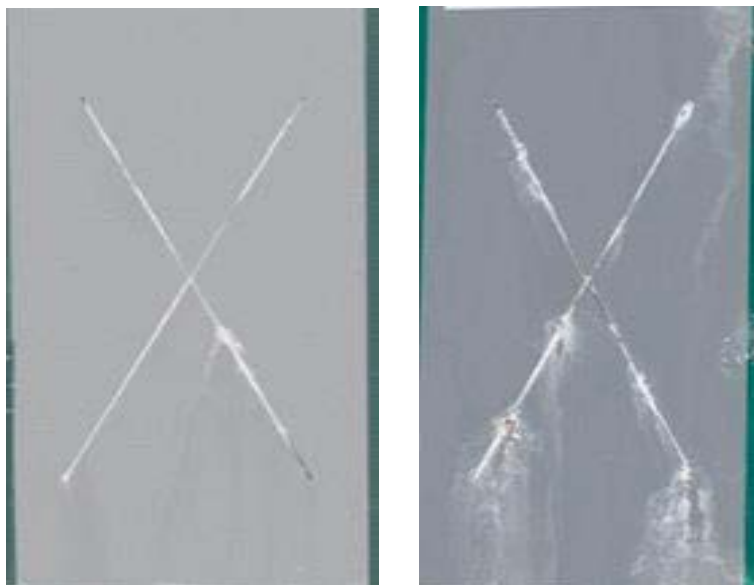
occurred on the MEH-PPV coated sample. The ratings given to the coating were 3,4,0 for scribe appearance, undercutting and blistering, respectively.

An overall rating of “acceptable” for a coating means that minor corrosion of no greater than 2 was observed. An overall rating of “low” means that minor corrosion of no greater than 2 and undercutting or blistering of no greater than 1 was observed. An overall rating of “poor” is any combination of ratings for corrosion, undercutting, or blistering that is greater than the two described above. The overall rating for the MEH-PPV system, which received scores of 3,4,0, was “poor”. For comparison, the scores for the Cr(VI)-based system were 2,0,0, and that coating received an overall rating of “acceptable”.

## 4. CONCLUSIONS

The following conclusions can be made from the laboratory testing of Cr(VI)-free aerospace coatings that incorporate an MEH-PPV pretreatment layer coated on AA2024-T3 substrates:

- MEH-PPV has adequate qualitative adhesion characteristics in aerospace coating systems,
- MEH-PPV coating systems show acceptable pull-off adhesion strength when compared to Cr(VI) control coating systems,
- MEH-PPV has an acceptable pencil hardness rating of HB at ambient conditions, which matches that of the Cr(VI)-based controls,
- Impact flexibility showed that MEH-PPV coated systems performed as well as Cr(VI) control systems,
- Xenon-arc testing (500 hours) of MEH-PPV coating systems resulted in a color change of  $\Delta E = 0.6$ , which



**Figure 3:** Cr(VI) coated coupon controls (left-side) vs. MEH-PPV coated coupons (right-side).

again matches the performance of the Cr(VI) based controls,

- MEH-PPV as pretreatment coating with a non-Cr(VI) primer and MIL-PRF-85285 Type IV topcoat failed the 2000 hours NSS exposure test.

Therefore, serious deficiencies in the MEH-PPV pretreatment performance as a corrosion protective coating, when compared to the Cr(VI) control systems, were observed. The MEH-PPV pretreatment coating incorporated into a non-Cr(VI) military aerospace coating cannot meet the United States Air Force requirements as an alternative to CCC.

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