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Electroactive Polymers as Environmentally Benign Coating Replacements for Cadmium Plating on High Strength Steels

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Naval Air Warfare Center Weapons Division
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For:

The Strategic Environmental Research and Development Program

Report Documentation Page

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List of Acronyms

ATR-FTIR	Attenuated total reflectance FTIR
DI water	deionized water
EAP	electroactive polymer
EDAX	energy dispersive X-ray analysis
EDOT	3,4-ethylenedioxyrthiophene
EIS	electrochemical impedance spectroscopy
FA	ferric acetylacetonate
FC	ferric citrate
FO	ferric oxalate
IVD Aluminum	ion vapor deposited aluminum
MS	mass spectroscopy
3MT	3-methylthiophene
3MOT	3-methoxythiophene
NR	no reaction
NMR	nuclear magnetic resonance
NFS	notched fracture strength
OCP	open circuit potential
P3HT	poly(3-hexylthiophene)
P3PPA	poly(3-pyrrol-1-yl) propanoic acid
3PPA	3-(pyrrol-1-yl) propanoic acid
3PPN	3-(Pyrrol-1-yl) proprionitrile
SEM	scanning electron microscopy
SERDP	Strategic Environmental Research and Development Program
TC	thiophene acetic acid
TP	thiophene methyl phosphonate

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Acknowledgements

Executive Summary

Despite environmental hazards, cadmium (Cd) is still widely used in the plating industry (especially for fasteners) because of its unique combination of properties. There is no drop-in replacement for Cd-plated high-strength steels, but commercial zinc (Zn) and aluminum (Al)-filled polymers deposited by the dip-spin coating technique have shown initial promise. Although they are quite effective, the coating tends to clog fastener threads, and their torque characteristics tend to change over the course of multiple assemblies. This is a serious drawback for aerospace and other DoD applications where weapon systems require periodic strip-down and maintenance. In order to meet the environmental challenge of replacing Cd on high strength steel substrates without the loss of performance, a novel approach using electro-active polymers (EAP's) as the corrosion inhibition layer has been investigated.

Several of the objectives of this SERDP SEED have been accomplished successfully. The synthesis and characterization of new monomers and the synthesis, using electroless deposition techniques, of EAPs that adhere to steel substrates has been completed. Electroless deposition is a non-line-of-sight coating onto steel plates and other geometries. The characterization of critical coating properties, using a combination of standard methods for fastener performance such as galling testing and hydrogen embrittlement testing, along with an evaluation of corrosion performance using impedance spectroscopy and neutral salt fog testing, has also been completed.

The results to date (summarized below) demonstrate that the program has achieved several of the objectives

- The new polymeric materials contain no heavy metals (Cd, Cr, Ni, Zn, Cu, etc.).
- New and known monomers, polymers and co-polymers were prepared and processed to produce thin films on steel substrates.
- Thiophene-based co-polymers with adhesion promoting groups have been formed into good quality films by solvent casting and exhibit good adhesion properties.
- Aqueous electroless deposition of pyrrole-based polymers containing adhesion promoting groups has been demonstrated.
- The EAP electroless deposition coating process does not introduce hydrogen into the specimens nor lead to hydrogen enbrittlement during environmental exposure.
- EAP polymers with hard particle additives have measured galling resistance values of 6000-8000 psi, not as good as cadmium but superior to coatings such as IVD aluminum
- None of the polymer samples have passed 96 hr neutral salt fog test to date, mainly due to insufficient film uniformity. The essential characteristics of the EAPs that lead to improved film quality have been identified and will be incorporated into all future EAP materials.

In conclusion, the program has resulted in the acquisition of basic knowledge regarding synthesis techniques and the relationship between material composition and critical coating properties in EAPs for replacement of cadmium coatings on high strength steels. The application of this knowledge will enable the development of an optimal EAP coating that can serve as an effective environmentally benign replacement.

Objectives

In order to meet the environmental challenge of replacing cadmium (Cd) on high strength steel substrates without the loss of performance, a novel approach using EAPs was investigated. The objectives include: (a) synthesis and characterization of new monomers; (b) synthesis, using electroless deposition techniques, of EAPs that will adhere to steel substrates and demonstrate non-line-of-sight coating onto steel plates and fasteners; (c) demonstration of comparable corrosion resistance using accelerated weathering tests (Neutral Salt Fog ASTM B117) with Cd-plated high-strength steel coupons as control samples, measurement of barrier properties using electrochemical impedance spectroscopy (EIS) and examination for evidence of passivation of steel substrates using a combination of scanning electron microscopy (SEM) with energy-dispersive-X-ray analysis (EDAX); and finally (d) measurement of other critical coating properties using a combination of standard methods for fastener performance such as galling testing (ASTM G98) and hydrogen embrittlement testing (ASTM F519 and F1624).

Background

The extensive use of cadmium in industrial operations such as smelting and refining of zinc, lead, copper ores, electroplating, welding, manufacture of pigments, plastic stabilizers and nickel-cadmium batteries has resulted in worker exposure to cadmium [1]. Cadmium exposure can result in pulmonary carcinogenesis, tumors of the prostate, testes and hematopoietic system [2,3]. Cadmium that is released into the environment through human endeavors can contaminate food, water and air. Cadmium can leach through soils into the groundwater where it can bind to river sediment and bioaccumulate. Cadmium does not break down in the environment and can accumulate in the food chain. Cadmium is a carcinogen and a tetragen and is highly regulated by the EPA [4].

Despite these environmental hazards, Cd is still widely used in the plating industry (especially for fasteners) because of its unique combination of properties. Cadmium plating has a unique combination of properties that makes it highly attractive for military use [5]. Several high-strength steels used by the military and commonly cadmium-plated for fastener applications include, but are not limited to the following: AISI 4340, Hy-Tuf℧ (an AISI 4340 derivative created by Crucible Specialty Metals), Aermet℧ 100, E4340, M50, 300M, PH 13-8Mo stainless steel, and maraging Grades 200 – 250.

The most common method of electroplating cadmium onto high strength steel is the alkaline cyanide bath. While this technology ranks as one of the oldest for cadmium plating, it is also the most forgiving and reliable plating solution, and presently proposed replacements have difficulty in matching its performance (See Table 1) [6-12]. As stated earlier there are no drop-in replacements for Cd-plated high-strength steels, but the Dacromet, Geomet and Magni families of coatings have shown initial promise. These materials are commercial zinc (Zn) and aluminum (Al)-filled polymers deposited by the dip-spin coating technique, and are often used for automotive applications. Although they are quite effective, the coating tends to clog fastener threads, creating installation problems. In addition, their torque characteristics tend to change over the course of multiple assemblies. This is not a problem for cars but it is a serious drawback for aerospace and other DoD applications where weapon systems require periodic strip-down and maintenance.

Table 1. Cadmium Replacements Suggested by Military, Commercial or Governmental Working Groups for High Strength Steel Fasteners [6-12].

Proposed Replacement	Organization	Possible Limitations
Ion vapor deposited (IVD) aluminum	Air Force	Line-of-sight process, holes not thoroughly coated
Sputtered aluminum	Air Force	Coating tends to gall
Tin/Zinc electroplating	Air Force	Difficult to control process
Zinc/nickel electroplating	Army	Nickel is an EPA regulated material; requires special chromate treatment
Tin/zinc electroplating	Army	Difficult to control process
Stainless steel with no coating	Army	Corrosion of carbon steel (galvanic effect)
Electroplated zinc	Army	Voluminous white corrosion products
SermeTel® (Sermatech Inc)	Navy	Performance hindered by complex geometries
Zinc/nickel with E-coat topcoat	Navy	Performance hindered by complex geometries
Zinc electroplate-alkaline bath	Navy	Better than acid-bath zinc
Zinc electroplate-acid bath	Navy	Does not perform as well as alkaline bath zinc plating
Dacromet 320/500® L/B	DoD	None listed
Boeing zinc-nickel electrodeposition	Commercial	Nickel is an EPA regulated material; requires special chromate treatment
Aluminum electroplating (Aluminplate)	DoD	Complicated application process
Aluminum manganese	DoD	Relatively expensive; inadvertent water in the bath creates HCl
Geomet® L	Commercial	None listed
Magni 511®	Commercial	None listed
Tin-nickel	DoD	Nickel is an EPA regulated material

In order to meet the current specifications for high-strength steel fasteners, our efforts will focus on using electroactive polymers as replacements for cadmium coatings. Electroactive polymers–specifically polyaniline (PANI)-have been shown to provide corrosion protection of steel alloys [13,14]. The Los Alamos National Laboratory (LANL) and the John F. Kennedy Space Center (KSC) team demonstrated that doped PANI coatings inhibited corrosion in carbon steel. The LANL-KSC work was based on earlier work by Jain et al. [15], in which the corrosion protective properties of EAPs were hypothesized. Jain's hypothesis was based upon the idea that the interfacial contact between a metal surface and a doped EAP would generate an electric field that would restrict the flow of electrons from the metal to the outside oxidizing species. This process would thereby reduce or prevent corrosion. The LANL-KSC researchers demonstrated this idea by coating 0.05-cm thick films of PANI doped with p-toluenesulfonic acid onto carbon steel and exposing these samples to 3.5 wt% NaCl/0.1M HCl solutions. The PANI coat was covered with an epoxy topcoat and compared to epoxy topcoat alone. The PANI-epoxy topcoat samples performed significantly better than the epoxy topcoat alone. These initial studies were used as

the foundation to develop EAP coatings to protect the ground support equipment from the corrosive effects of acid vapor generated during shuttle launches.

The mechanism of corrosion protection by EAPs, specifically PANI has been identified as both barrier protection and passivation of the metal alloy [16,17]. Thus EAPs also can serve as passivating coatings. EAPs have been shown to perform successfully in acidic [13,14], neutral and alkaline environments [18,19]. This combination of barrier and passivation protection is a significant technical advance over the sacrificial mechanism of the older cadmium, aluminum and zinc coatings. It avoids coating dissolution, together with the problems caused by corrosion products causing component seizure, lifting paint, and causing unsightly marks. The use of EAPs is not just a Cd alternative, but provides a new mechanism that could be incorporated more broadly into the entire DoD corrosion protection arsenal, including non-chrome primers and paints. Unlike Cd plating, it might ultimately even be applied by enlisted personnel in the field.

EAPs other than PANI have also been demonstrated to protect steel alloys in harsh environments. Poly(3-methylthiophene) (P3MT) films coated onto platinum and 430 stainless steel showed effective stabilization of the steel in a passive state [20]. P3MT films coated onto a 430SS rotating disk electrode (RDE) in 1N sulfuric acid solution showed galvanic protection. This protection was described by DeBerry [21], using a mechanism in which the P3MT film stabilizes the passive layer by providing a transient current to heal small defects inside the passive film before they could expand. Recently, Naval Air Warfare Center Weapons Division (NAWCWD) researchers have shown quantitative evidence that EAPs, specifically poly(2,5-bis-N-methyl-N-hexylamino)phenylene vinylenes (BAM-PPV) can provide corrosion protection for 2024 Al alloys in simulated marine environments [18] and BAM-PPV coated onto 2024 Al panels showed similar performance to chromate conversion coated 2024 Al panels up to 336 hours of neutral salt-fog tests[22].

Materials and Methods:

Materials and General Analytical Methods

3-(Pyrrol-1-yl) proprionitrile (3PPN), sodium hydroxide (NaOH), 3,4-ethylenedioxyrthiophene (EDOT) and 3-aminopropyltrimethoxysilane were purchased from Aldrich and used as received. Iron (III) chloride (FeCl$_3$), iron(III) chloride hexahydrate (FeCl$_3$*6H$_2$O), ferric citrate (FC) (FeC$_6$H$_5$O$_7$), iron(III) acetylacetonate (FA) (Fe(C$_5$H$_7$)$_2$)$_3$, iron(III)oxalate hexahydrate (FO) (Fe(C$_2$O$_4$)$_3$*6H$_2$O, sodium thiosulfate (Na$_2$S$_2$O$_3$*5H$_2$O) and ammonium thiosulfate (NH$_4$)$_2$S$_2$O$_3$ were purchased from Aldrich and used as received.

^{1}H and ^{13}NMR spectra were acquired using a Bruker Avance 400 MHz NMR spectrometer. Mass spectra data were obtained using a JEOL thermal desorption mass spectrometer (TD-MS). Thermal analysis data on selected polymers were obtained via Differential scanning calorimetry (DSC) using a TA Instrument 2910 DSC and Thermogravimetric analysis (TGA) was conducted using a TA Instruments 2950 TGA. Melting points (m.p) were measured with a Melt-Temp and are uncorrected.

The FTIR measurements were made using a Nicolet Nexus 870 FTIR spectrometer with a liquid nitrogen cooled MCT detector. Each spectra is an average of 128-256 scans with 4 cm^{-1} resolution. The monomer and polymer bulk samples were analyzed using a "Thunderdome" attenuated total reflectance (ATR-FTIR) accessory with a germanium crystal. The samples adsorbed on a surface were analyzed using specular reflectance. The incoming radiation was at 80° with respect to the surface normal.

The particles used in the particle coating operation included (1) Monarch 900 carbon black (an organic pigment containing ~50% graphite, dispersed as ~1 :m particles), (2) molybdenum sulfide (99%, supplied from Aldrich Chemical as particles of less than 2 :m size) (3) fumed silica, supplied Aldrich as particles significantly less than 1 :m in average size, and (4) boron carbide, supplied from Aldrich as particles approximately 10 :m in average size.

Galling testing was performed in accordance with specification ASTM G98, which required galling testing performed with button and block specimens. These specimens were manufactured from AISI 4340 steel hardened to 50 – 55 HRC (representing high-strength steel). A group of button specimens were plated with cadmium (in accordance with SAE-AMS-QQ-P-416, Type II, Class 2), while others were coated with IVD aluminum (in accordance with MIL-DTL-83488, Type II, Class 2) for comparison to the polymer samples. In addition, fixtures were required that conformed to the dimensions listed in ASTM G98 for galling testing. These fixtures included a support cylinder and a plate support fixture. These were also fabricated from high-strength steel.

To evaluate the resistance of different polymer film coatings as a replacement for cadmium, Cd-plated specimens per Federal Specification QQP-416, Type II, Class 1 were used as a baseline. Bare metal (uncoated) specimens were first tested in air per ASTM F519/F1624 to measure any residual hydrogen due to manufacturing of the specimens.

Testing at ASTM E8 (fast fracture) loading rates provided the limiting value in that insufficient time is not allotted for hydrogen diffusion to occur and cause any damage. The average value of the Notched Fracture Strength in bending, NFS(B), of the specimens obtained from certification testing of the specimens was designated as 100% NFS.

Testing in air at ASTM F1624/G129 slow loading rates provided sufficient time for hydrogen diffusion to occur to provide a quantitative measure of residual hydrogen in the as-manufactured steel specimens. RSL™ testing was used to measure the *threshold* for the onset of hydrogen embrittlement in accordance with ASTM F519 for Type 1e specimens. The average value of NFS(B) that was the limiting value of the hydrogen embrittlement *threshold* in the certification tests was 91.6 % NFS.

Methods:
Synthesis Section

Small-scale preparation of 3-(pyrrol-1-yl) propanoic acid (3PPA)(Figure 1)[23]

A 250 mL round bottom flask was equipped with a reflux condenser and nitrogen inlet/outlet valve. The round bottom flask was charged with 50 mL deionized water (DI water) and 13.3 g NaOH pellets. After addition of the NaOH pellets the solution became turbid. After 5 minutes, the solution became clear and homogenous. The 3-(pyrrol-1-yl) proprionitrile (10.0 g, 83.2 mmol) was added to the reaction flask and the solution was refluxed for 12 hours under a positive nitrogen pressure. After 12 hours the solution was homogenous and orange colored. There was no ammonia evolution from the top of the condenser as measured by moist pH paper. Cold DI water (25 mL) was added and the solution and was cooled to ambient temperature. The reaction flask was placed in and ice/water bath and 14 mL of a 50% aqueous sulfuric acid solution (1:1, v/v) was added slowly. The solution was stirred and a semi-solid formed immediately. The contents of the reaction flask were extracted 3X with ether and the ether layer separated from the aqueous phase. The ether layer was dried over magnesium sulfate and the solution filtered. The filtrate was rotovapped to a semi-solid residue and dried in a vacuum dessicator (0.05 Torr, 25EC) for 12 hours. An off-white tan product was obtained in 35% yield (4.0 g), m.p = 45-47EC (uncorrected, literature value = 59-60EC). ^{1}H NMR (DMSO-d$_6$): 2.67 (t, 2H); 4.09 (t, 2H); 5.95 (t, 2H) and 6.73 (t, 2H), 13C NMR (DMSO-d$_6$): 36.05, 44.40, 107.5, 120.4 and 172.3. FTIR: 3000 cm^{-1} broad (OH stretch), 1710 cm-1(C=O stretch). Identified with thermal desorption-MS: molecular peak at 138.9 amu.

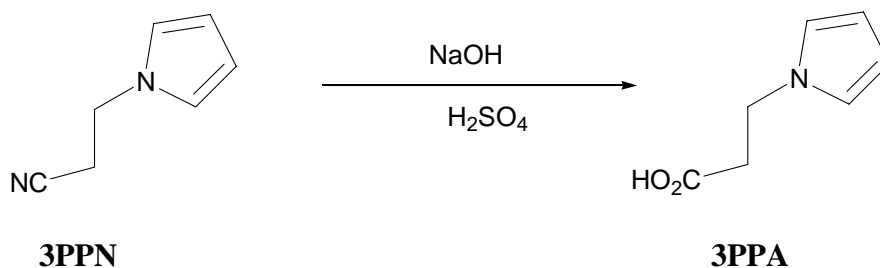**3PPN**　　　　　　　　　　　　　　　　　　**3PPA**

Figure 1.　Synthesis of 3-(pyrrol-1-yl) propanoic acid (3PPA).

Scale-up of 3-(pyrrol-1-yl) propanoic acid (3PPA): A 500 mL 3-neck round bottom flask was equipped with a reflux condenser and nitrogen inlet/outlet valve. The round bottom flask was charged with 200 mL DI water and 40 .0g NaOH pellets were added slowly with stirring to the reaction flask. After 10 minutes the solution was homogenous, and 3PPN (30.0 g, 249.7 mmol) was added to the reaction flask. The solution was refluxed for 12 hours under a positive nitrogen pressure. After 12 hours, the solution was homogenous and orange colored. There was no ammonia evolution from the top of the condenser as measured by moist pH paper. Cold DI water (100 mL) was added and the solution was cooled to ambient temperature. The reaction flask was placed in an ice/water bath and 100 mL of a 50% aqueous HCl acid solution (1:1, v/v) was added slowly to acidify the reaction mixture (pH =2). The solution was stirred and a semi-solid formed immediately. The solid was removed via filtration and the filtrate was extracted 3X with ether and the ether layer separated from the aqueous phase. The ether layer was dried over magnesium sulfate and the solution filtered. The filtrate was rotovapped to a semi-solid residue and both solid materials were dried in a vacuum dessicator (0.05 Torr, 25 EC) for 12 hours. Each solid was obtained as an off-white/tan product and the combined weight gave nearly quantitative yield (33.4g, 98%). Both products were each identified as the monomer (3PAA) via ^{1}H and ^{13}C NMR.

Chemical Polymerization of Thiophene Based Monomers (Figure 2): Because some of the chemical oxidants are not commonly used as such, several monomers (EDOT, 3MT, and 3MOT) known to readily undergo chemical oxidative polymerization were used for comparison with the lesser-known monomers (TC and TP; PyC was not available at the time the chemical polymerizations wee attempted.) Oxidants used were ferric chloride ($FeCl_3$, as a control), ferric citrate (FC), ferric oxalate (FO), and ferric acetylacetonate (FA). All the monomers were soluble or miscible in propylene carbonate as well as in methanol, but the same was not true for the oxidants. $FeCl_3$ and FA are both readily soluble in both propylene carbonate and methanol, but FC and FO are insoluble in both solvents. FO is fully soluble in water, but FC is only partially soluble in water. Reactions are summarized in Table 2, where NR indicates no reaction, and P indicates polymerization occurred; numbers in parentheses are reaction identification numbers. The only definitive case of polymerization was of EDOT polymerizing with $FeCl_3$ in propylene carbonate (as expected); EDOT may have polymerized in aqueous FO, but further analysis is needed to be sure. In two cases, reactions 4 and 10, no reaction was immediately evident, but upon stirring overnight, changes occurred that might be indicative of polymerization; further analysis is needed to be sure. None of the new oxidants appears particularly successful; FC didn't induce polymerization in any case, and FA and FO results are mediocre at best. Neither of the new monomers appears to polymerize via chemical oxidative polymerization (with the possible exception of TC in $FeCl_3$). For thoroughness, reactions 4, 10, and 12 would need to be repeated and analyzed further.

Synthesis of Thiophene Derivatives: One of the target materials is a random copolymer of thiophene acetic acid with hexylthiophene to produce a soluble polymer with good adhesion properties. While thiophene acetic acid (TC) is commercially available, it had to be esterified to be incorporated into the random co-polymer. The esterification was readily performed with methanol and an acid catalyst. The ester and hexylthiophene were chemically polymerized with iron chloride to yield the polymer in good yields. By NMR analysis, the ester was incorporated into the polymer at between 10 and 15%. The polymer was then treated with base followed by

acid to obtain the polymer with free carboxylic acid groups to promote adhesion. This polymer was then spray-cast from toluene onto clean steel 1008 panels. After flash drying at 200 °C for 10 min, the polymer passed the dry tape test for adhesion.

The next target material is a random copolymer of thiophene methyl phosphonate (TP) with hexylthiophene to produce a soluble polymer with good adhesion properties. The synthesis began with the available thiophene methanol, which was converted to thiophene methyl chloride with concentrated hydrochloric acid. The thiophene methyl chloride was treated with triethyl phosphite to yield the diethyl thiophene methyl phosphonate. The material was purified by distillation and polymerized as above. By NMR analysis, the ester was incorporated into the polymer in about 10%. This polymer was then spray-cast from toluene onto clean steel 1008 panels. After flash drying at 200 °C for 10 min, the polymer passed the dry tape test for adhesion.
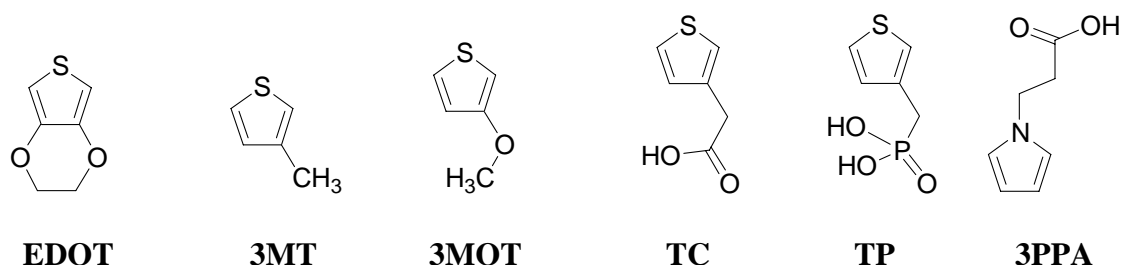
EDOT	3MT	3MOT	TC	TP	3PPA

Figure 2. Monomers for electroless and electropolymerization.

Table 2. Attempts at chemical polymerization.

| Monomer | Methanol | | | | Propylene Carbonate | | | | Water | |
	FC_{insol}	FO_{colors}	FA_{sol}	$FeCl_{3sol}$	FC_{insol}	FO_{insol}	FA_{sol}	$FeCl_{3sol}$	FC_{sol}	FO_{sol}
EDOT			NR (1)					P (2)	NR (11)	P? (12)
3MT	NR (7)						NR (8)			
3MOT			NR (9)				NR? (10)			
TC		NR (3)						NR? (4)	NR (13)	
TP			NR (5)					NR (6)		

Electrochemical Polymerization of Monomers: All six monomers were polymerized electrochemically (10mM monomer in 100mM TBABF$_4$/CH$_3$CN.) Results are tabulated below (Table 3). Electrochemistry of EDOT, 3MT, and 3MOT has been previously reported; all polymerize nicely in the electrolyte solution used here. 3MT polymerization occurs exactly as expected. 3MOT polymerization (Figure 3) is also perfectly normal. Notice the onset of monomer oxidation is somewhat lower than for 3MT (1.02 vs. 1.32V vs. Ag/Ag+); this is due to electron donation from the ether group. TC and TP do not polymerize in the stability window of acetonitrile; see Figure 4 for an attempt to electropolymerize TP. The constant current response seen in Figure 4 over multiple redox cycles is characteristic of acetonitrile. 3PPA, on the other

hand, polymerizes quite well electrochemically, as can be seen in Figure 5. 3PPA undergoes a very well-behaved, reproducible electropolymerization. A linear increase in peak current as a function of scan rate is observed for P3PPA, indicating that the film is electrode supported and electroactive.

Table 3.   Results of electrochemical polymerization attempts.

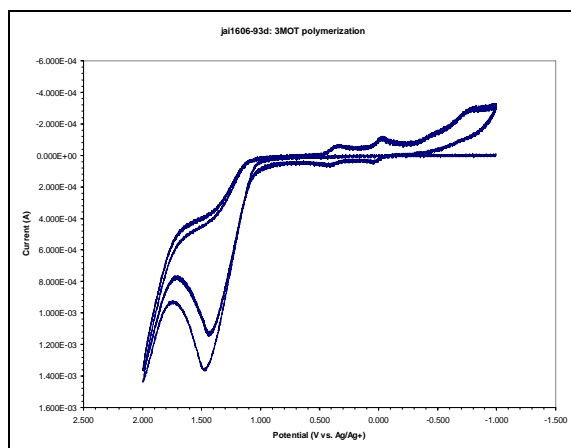| Monomer	Eon,m (V vs. Ag/Ag$^+$)	Ep,m (V vs. Ag/Ag$^+$)
EDOT	0.78	-
3MT	1.32	ca. 2.0
3MOT	1.02	1.44
3PPA	0.84	1.25
TC	no polymerization evident	
TP	no polymerization evident	

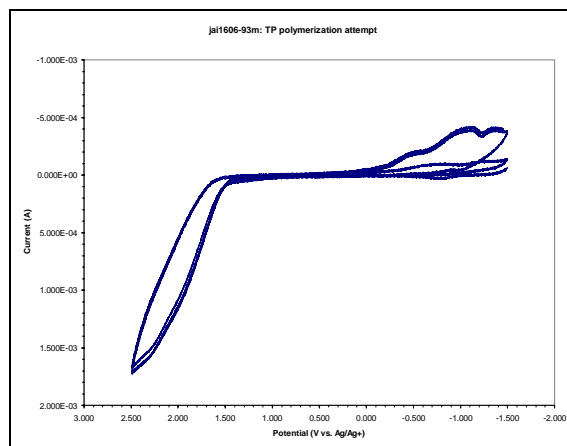**Figure 3.   Electropolymerization of 3MOT.**

Figure 4.   Attempt to polymerize TP.
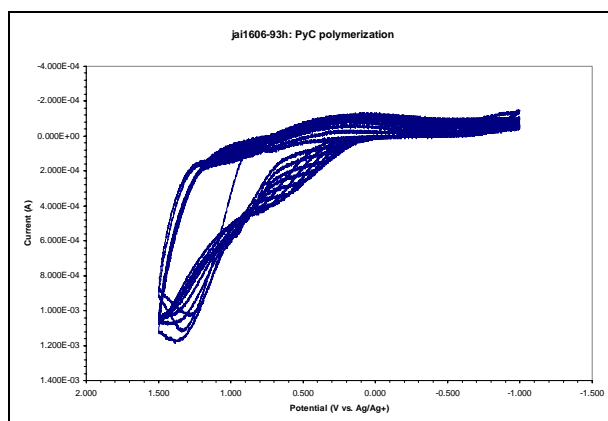

Figure 5. Electropolymerization of 3PPA.

<u>Electroless Deposition of 3PPA:</u>[24] The electroless deposition (non line-of-sight) of the monomers utilized in this study was based on a prescreening process using the electropolymerization results described previously, based on the principle that the monomers with the lowest oxidation potential would undergo facile electroless polymerization. Since 3PPA does undergo electropolymerization at a low potential, it is a candidate for the electroless deposition. The electroless deposition consisted of 3 steps using the 3PPA monomer.

Step I: The high strength steel substrate (4340) [3x3x0.25; 3x6x0.25, galling specimens and defect tolerance specimens] were cleaned using toluene, acetone, methanol and isopropanol to remove grease, dirt and any other debris that may be present on the sample. The samples were then air dried for 15 minutes prior to deposition. No evidence of corrosion was visible during this stage of the electroless deposition process.

Step II: The cleaned sample was placed in a Pyrex glass dish (size depended on sample dimensions) and a 0.5 wt %/vol. of 3-aminopropyltrimethoxy silane solution was added to the samples. The samples were allowed to stand in the silane solution for 5 minutes after which time

the samples were removed and dried in a vacuum oven (28 in Hg, 100EC).   After one hour, the samples were removed from the oven and allowed to cool in a dessicator for one hour. The steel samples were measured with FTIR to determine if the silane had reacted with the substrate. A very thin layer of 3-aminopropyltrimethoxysilane deposited on a stainless steel surface is shown in the spectrum (Figure 6) confirming the presence of the silane on the surface before the polymer deposition.
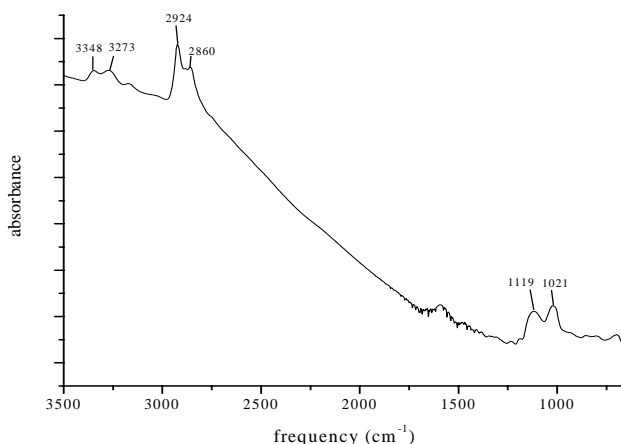

Figure 6.   3-aminopropyl trimethoxysilane on stainless steel button.

Step III: The silanated sample was then placed back into the Pyrex glass dish for the polymerization deposition process.   Numerous attempts using a variety of solvents, (e.g DI water, methanol) and oxidants (FeCl$_3$, FeCl$_3$*6H$_2$O, FeC$_6$H$_5$O$_7$, Fe(C$_5$H$_7$)$_2$)$_3$, Fe(C$_2$O$_4$)$_3$*6H$_2$O, Na$_2$S$_2$O$_3$*5H$_2$O and (NH$_4$)$_2$S$_2$O$_3$) were tried. The oxidants FeCl$_3$ and FeCl$_3$*6H$_2$O performed the best during the polymerization. Several different molar concentrations of the monomer in DI water were examined during the deposition (0.03M, 0.25M, 057M).   The 0.25M solution of 3PPA and oxidant FeCl$_3$ at a concentration of 0.67M were found to be the optimum conditions for the electroless deposition process.   Both the monomer solution and oxidant solution were added simultaneously to the Pyrex dish containing the steel samples. The solution was briefly agitated (<5 minutes) and covered and allowed to react at ambient temperature for 6 hours. After 6 hours a black film was present on the substrate. The substrate was dried in a vacuum oven (28 in Hg, 70°C) for 6 hours. After 6 hours of drying time, the substrate was removed from the oven and cooled to room temperature in a dessicator. The identification that the polymer (P3PPA) had reacted with the silane coated substrate was confirmed by FTIR.   The polymer deposited on a silanated surface is shown in Figure 7. It is different from the bulk polymer sample (as prepared using FeCl$_3$ in DI water and purified after polymerization)(Figure 8). Peaks at ~ 3440, 1593, and 1539 cm^{-1} are indicative of the N-H stretch, amide I and amide II bonds, respectively, of a secondary amide. The carbonyl peak of the carboxylic acid group at 1710 cm^{-1} decreased in intensity, indicating that it's concentration decreased significantly. Thus, the polymer during the electroless deposition underwent a reaction at the surface with the amino-silane that was on the

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surface to form the amide. The polymer is deposited on the surface as a non-uniform film, with a general thickness range from 2-30 microns. The polymer (P3PPA) does show brittleness with some flaking off of the material.
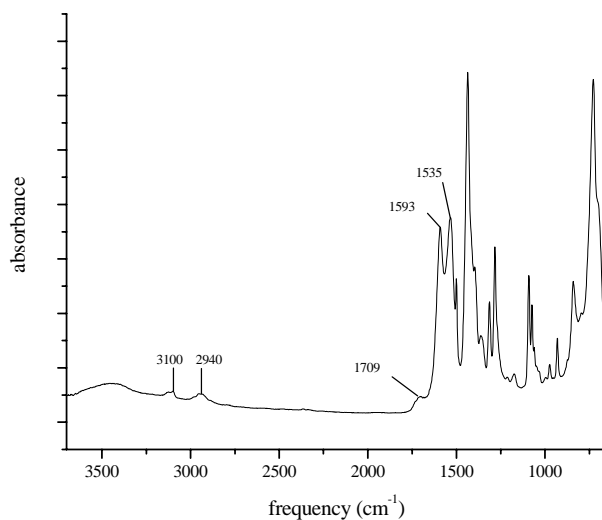
Figure 7.   P3PPA deposited on steel substrate.

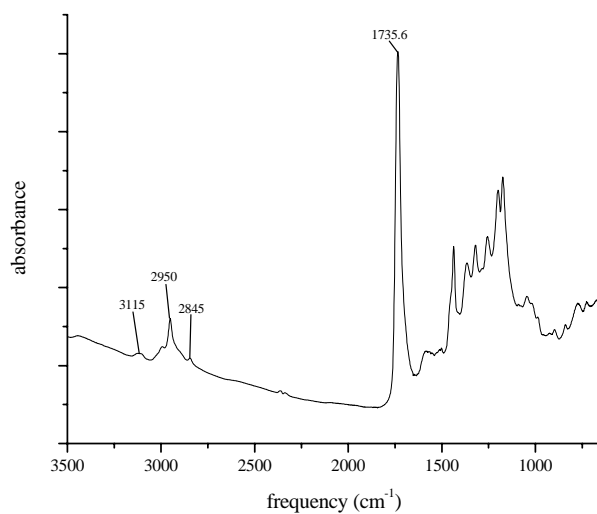**Figure 8.   Bulk P3PPA.**

Galling testing: Galling testing was performed in accordance with specification ASTM G98, which required galling testing performed with button and block specimens. These specimens were manufactured from AISI 4340 steel hardened to 50 – 55 HRC (representing high-strength steel). A group of button specimens were plated with cadmium (in accordance with SAE-AMS-

QQ-P-416, Type II, Class 2), while others were coated with IVD aluminum (in accordance with MIL-DTL-83488, Type II, Class 2) for comparison to the polymer samples. The remainder of the uncoated specimens were coated with various electroactive polymers. In addition, fixtures were required that conformed to the dimensions listed in ASTM G98 for galling testing. These fixtures included a support cylinder and a plate support fixture. These were also fabricated from high-strength steel.

Surface Roughness Testing: The surface roughness of the various buttons were measured in order to verify that they met the 10 to 45 :in guideline within the ASTM G98 specification. Table 4 displays the surface roughness averages of representative samples. The cadmium plating samples had a surface roughness outside of the desired range; however, it is believed this is the nature of the coating, and therefore unavoidable. Several different electroactive polymer coatings were compared to the IVD aluminum and cadmium plated samples. Several of the electroactive polymer samples were embedded with 2 μm diameter spherical particles for increased lubricity. These embedded samples showed higher surface roughness and greater variability than the samples that were coated with the polymer only. Some of the coatings behaved like greases, resulting in damage to the coating during surface roughness measurements, and therefore could not be measured.

Table 4. Average surface roughness measurements of coated steel buttons.

Coating	Button 1 Surface Roughness μin	Button 2 Surface Roughness μin	Button 3 Surface Roughness μin	Average Surface Roughness (Ra) μin
Cadmium	75.8	75.4	79.0	76.7
IVD Aluminum	32.2	38.4	33.4	34.7
P3PPA	43.2	50.5	45.3	46.3
P3PPA with graphite	96.7	177.9	192.5	155.7
P3HT MoS$_2$	N/A	N/A	N/A	N/A
P3HT	126.1	100.4	N/A	113.3
P3PPA+MoS$_2$	161.9	294.5	N/A	228.2
P3PPA+SiO$_2$	125.2	99.9	75.2	100.1
P3PPA	N/A	N/A	N/A	N/A
P3PPA + boron carbide	N/A	N/A	N/A	N/A

Galling Test Procedure: The galling test was performed in accordance with ASTM G98. The previously described buttons with a 0.5-inch diameter were used for testing. The procedure utilized a 10,000-lb Instron static frame load cell. Belleville spring washers were used as part of the setup in order to keep the load constant during the turning operation (Figure 9). The first round of testing was performed using buttons and plates coated with similar coatings. As a result, both of these coatings galled on themselves, and it was determined that testing should be performed with only the button plated with the test coating and the steel plate left uncoated. The galling threshold of the bare AISI 4340 steel was determined in order to measure the increased galling resistance provided by the coatings.
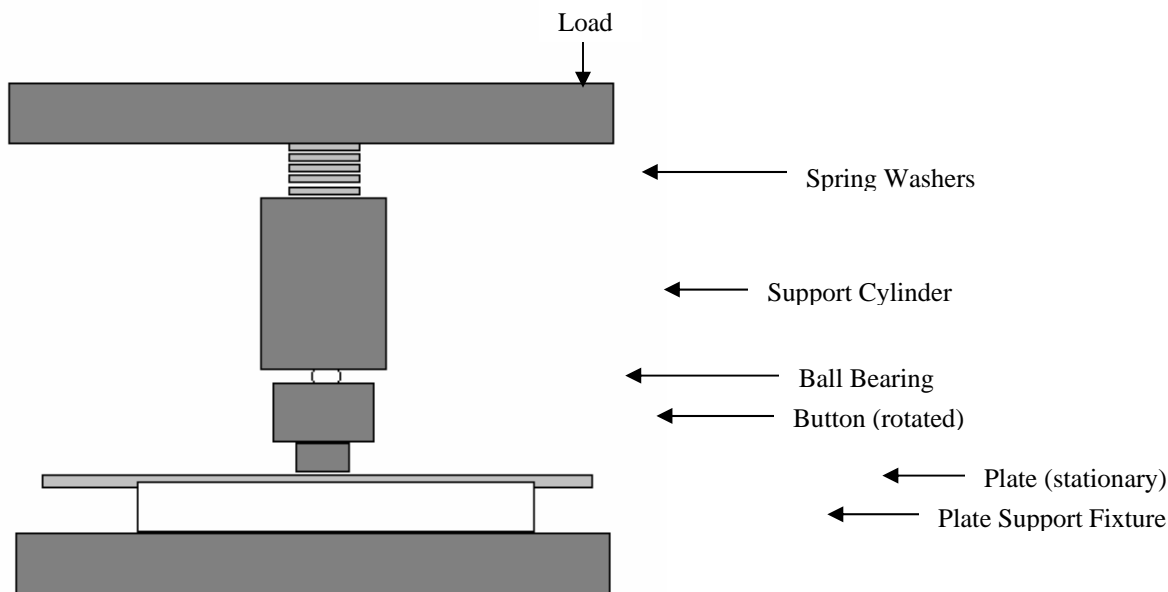
Figure 9. Schematic of galling test setup.

The test procedure consisted of the following:

i. Buttons and plates were cleaned ultrasonically with isopropyl alcohol. However, the alcohol disturbed some of the polymer coatings, so cleaning of the polymer coated buttons was omitted.

ii. The plate was placed in the support fixture so that an area free of surface defects could be used for galling testing.

iii. A button of the same coating material was loaded into the fixture with the ball bearing and support cylinder.

iv. An appropriate load was selected for testing

v. The button was rotated, using a modified tap wrench around the square bulk section, within the required 3 to 20 seconds, with an average of approximately 10 seconds.

vi. The load was released and the button and plate were examined for signs of galling.

vii. An appropriate load was chosen for further testing of the plating (if necessary) with a new button and a clean area of plate.

Hydrogen Embrittlement Studies

Baseline Evaluation Using Cd Plated Specimens: In order to evaluate the resistance of different EAP film coatings as a replacement for cadmium, Cd-plated specimens per Federal Specification QQP-416, Type II, Class 1 were used as a baseline. Bare metal (uncoated) specimens were first tested in air per ASTM F519/F1624 to measure any residual hydrogen due to manufacturing of the specimens. Testing at ASTM E8 (fast fracture) loading rates provided the limiting value in that insufficient time is not allotted for hydrogen diffusion to occur and cause any damage. The average value of the Notched Fracture Strength in bending, NFS(B), of the specimens obtained from certification testing of the specimens was designated as 100% NFS. The testing in air at ASTM F1624/G129 slow loading rates provided sufficient time for hydrogen

diffusion to occur to provide a quantitative measure of residual hydrogen in the as-manufactured steel specimens. RSLᴊ testing was used to measure the *threshold* for the onset of hydrogen embrittlement in accordance with ASTM F519 for Type 1e specimens. The average value of NFS(B) that was the limiting value of the hydrogen embrittlement *threshold* in the certification tests was 91.6 % NFS.

Degradation from Cd-plating: As a baseline for comparison to other coatings, specimens were Cd-plated per Federal Specification QQP-416 and tested in air at the same slow loading rate as the unplated specimens as a measure of any residual hydrogen due to the plating process. The *threshold* was found to be lowered from 91.6% to 85% NFS. This means that the bake out was inadequate in removing the hydrogen introduced into the steel during Cd-plating.

Environmentally Induced Hydrogen Stress Cracking (Hydrogen Embrittlement): The Cd-plating produces a galvanic couple with the 4340 steel specimen. The Cd-plating is anodic, sacrificially corroding relative to the steel; whereas, the steel is being cathodically protected with hydrogen being generated at its surface. Depending on the porosity of the Cd-plating, hydrogen will diffuse and be absorbed by the steel causing a degradation in strength with time. The Open Circuit corrosion Potential (OCP) of the Cd-plating in a 3.5% sodium chloride solution was measured against a Saturated Calomel Electrode to be -0.770 Vsce. By comparison, the steel specimen was -0.670 Vsce resulting in a difference in galvanic potential of 100mV. This difference in galvanic potential in salt water is the driving force for the generation of hydrogen on the surface of the Cd-plated 4340 steel specimen at 51 HRC. The RSL™ *threshold* per ASTM F519 is a measurement of the degradation due to immersion of a Cd-plated steel component in an marine salt water environment. The degradation, which is a measure of the susceptibility to hydrogen embrittlement, was found to be significant, reducing the fracture strength to 37.5% NFS(B) implying that the Cd-plating per Federal Specification QQP-416 is relatively porous even with the chromate conversion coating (The presence of chrome was verified with the SEM/EDX). A defect in the coating (holiday) causes a further reduction to 32.5% NFS(B) due to the direct exposure of the bare metal to the solution. No barrier exist due to the Cd-plating

Electrochemical Impedance Spectroscopy (EIS) Measurements: The corrosion behavior of the different samples (Cd plated and EAP coated 3x3x0.25) was evaluated in 0.5 N NaCl solution (open to air). EIS measurements were obtained at the open-circuit or corrosion potential E_{corr} in the frequency range of 100 KHz – 5mHz. The samples were exposed to the test solution for several days and measurements were taken as a function of time. A Gamry PCI4/300 potentiostat and Gamry EIS300 Software were used for the impedance measurements. The impedance spectra have been plotted as Bode plots, where the logarithm of the impedance modulus, |Z|, and the phase angle, M, are shown as functions of the logarithm of the frequency f of the applied ac signal.

Neutral Salt Fog Exposure: The Cd plated high strength steel coupons (3x6x0.25), bare metal and EAP coated coupons were placed in neutral salt fog chamber for corrosion performance evaluation on NAVAIR-AD racks (15E angle) in accordance with ASTM B117. Additional testing using EAP coated steel substrates (1008/1010) were examined for corrosion protection in neutral salt fog chambers.

Results and Accomplishments

Monomer synthesis and Polymerization Processes: The preparation of the monomers proceeded according to the literature recipes. The yields were high and reproducible. The structure determination of the monomers was accomplished via NMR, FTIR and MS analysis providing proof that the compound listed (Figure 2: TC, TP 3PPA) were obtained. The base polymers (thiophene and pyrrole) are inert with HMIS and NFPA rating of 0, 0 and 0 for health, flammability and reactivity.

The polymer applied onto steel substrates via air-brush and electroless deposition of the monomer does not introduce toxic materials into the bath. The process is benign and an environmentally green alternative to the current Cd plated baths for high strength steel. The process is portable, repeatable (though variation was seen in coating thickness and uniformity in the film) and a variety of substrate shapes and sizes can be coated via this non-line-of-sight electroless deposition process.

Hydrogen Embrittlement Studies/Defect Tolerance Testing: The Electroactive Polymer coating process does not introduce hydrogen into the specimens as compared to the Cd-plating. The Cd-plated specimen still had some residual hydrogen as determined by the 85.0% NFS(B) vs 91.6% NFS(B) (Table 5), where as the EAP coating of Lot #1 (P3PPA) and Lot #2 (P3PPA) was 90-95%, comparable to 91.6% for the baseline bare metal specimen.

Table 5. Resistance of Electroactive Polymer (EAP) (PPPA) coated specimens to Hydrogen Embrittlement.

	Cd-Plated %NFS	EAP Coated Lot #1 %NFS	EAP Coated Lot #2 %NFS	Baseline Bare %NFS
NFS(B)	NA	NA	NA	100
RSL™ *threshold* in Air	85.0	95.0	90.0	91.6
RSL™ *threshold* @ -0.80Vsce	37.5	46.5	47.5	NA
RSL™ *threshold* @ -0.80Vsce with holiday	32.5	49.0	59.5	NA

Cd-OCP = -0.770 Vsce in 3.5% NaCl Solution
Fe-OCP = -0.670 Vsce in 3.5% NaCl Solution
NFS = Notched Fracture Strength

The OCP of the Electroactive Polymer coating (Figure 10) is very close to the 4340 steel and therefore does not introduce hydrogen into the steel during environmental exposure due to the galvanic couple with the 4340 steel, as with the Cd-plating. Even with patches of the coating, it did not drive the mixed potential towards the more negative value of zinc (-1.1 Vsce), which could lead to environmentally induced hydrogen embrittlement.
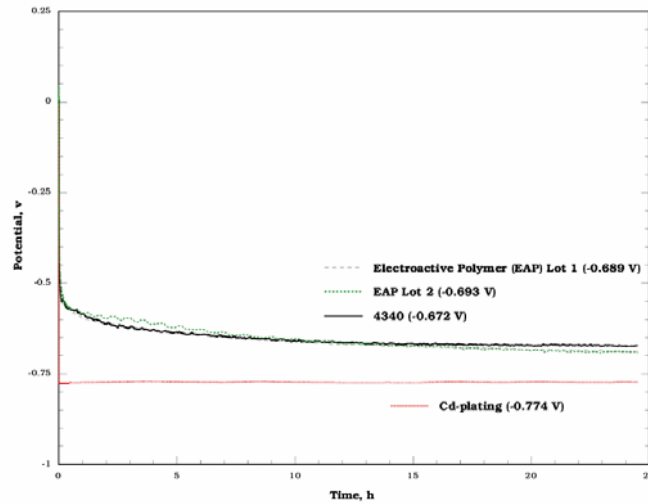
Figure 10.   Overlay plot of OCP tests results.

Galling Testing Results: The uncoated button and plate were tested first in order to determine an approximate threshold galling stress for uncoated AISI 4340 steel. Once the threshold was established, the various coatings were tested to see how much galling protection each provided. The load frame used for this test had a maximum load of 10,000-lbs, which equates to a stress of 51 ksi on the button. If galling did not occur at the maximum load, a value of 51+ ksi was recorded as the threshold galling stress. The uncoated AISI 4340 steel began to gall at a stress of approximately 10 ksi. Figures 11 and 12 show the results of this testing.
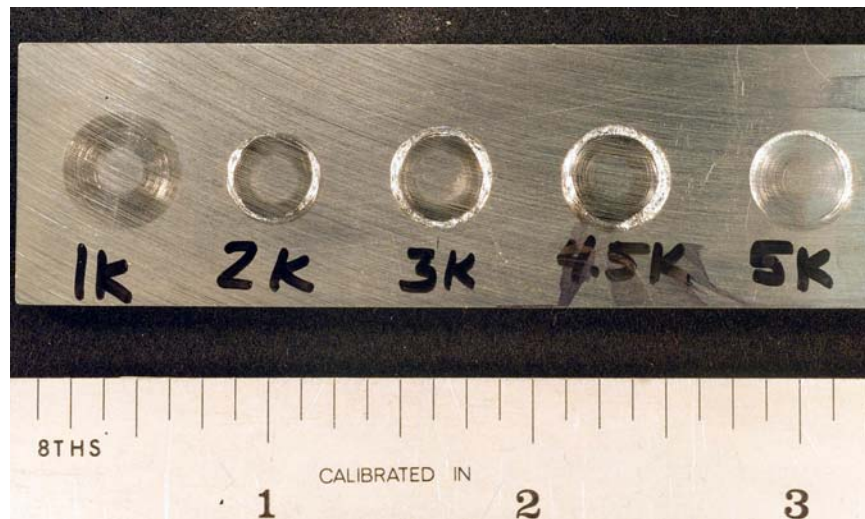

Figure 11.   AISI 4340 steel plate subjected to galling testing with uncoated steel buttons, showing galling between 1000lbs and 2000lbs (5ksi to 10ksi).
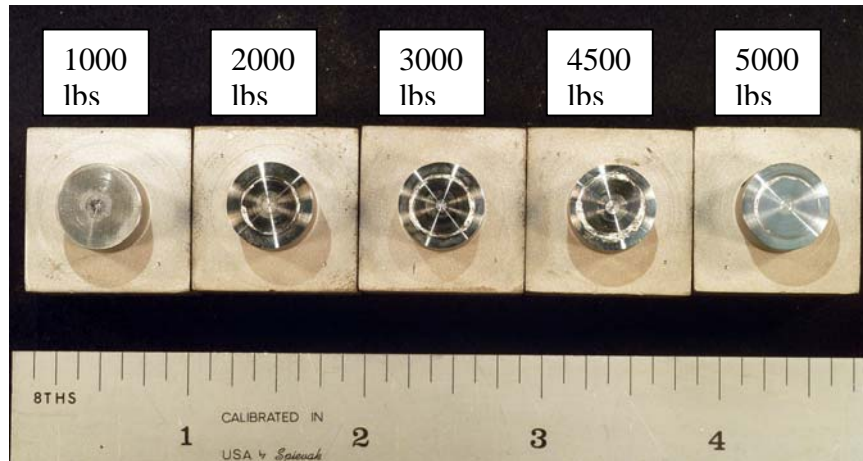
17

Figure 12. AISI 4340 steel buttons tested for galling on a steel plate (shown in Figure 11), displaying galling between 1000lbs and 2000lbs (5ksi to 10ksi).

The cadmium plated buttons were tested for galling resistance against the bare AISI 4340 steel plates. Cadmium is considered a gall resistant coating; therefore, cadmium on steel was tested at a starting stress of 10 ksi (2,000-lbs). After each test, the load was raised incrementally by 1,000-lbs until galling was noted. After each test, smearing and transfer of the cadmium was noted, but no galling was observed. At the maximum load of 10,000-lbs, no galling was noted and a maximum threshold galling stress of 51+ ksi was recorded. Figures 13 and 14 show the results of this testing.
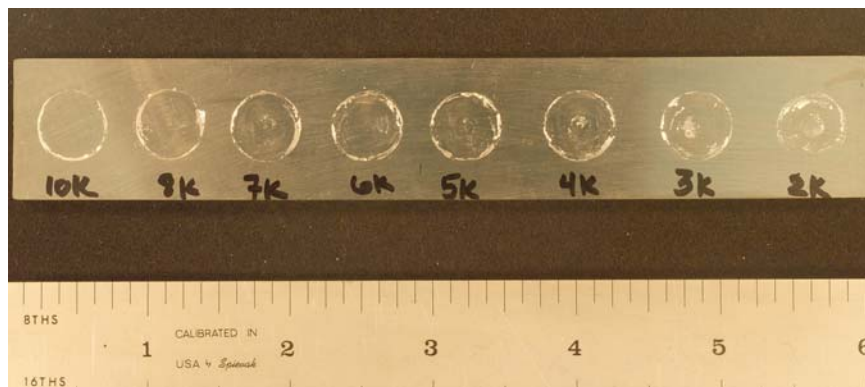

Figure 13:   AISI 4340 steel plate subjected to galling testing with cadmium plated steel buttons, showing no galling at a maximum load of 10,000lbs.
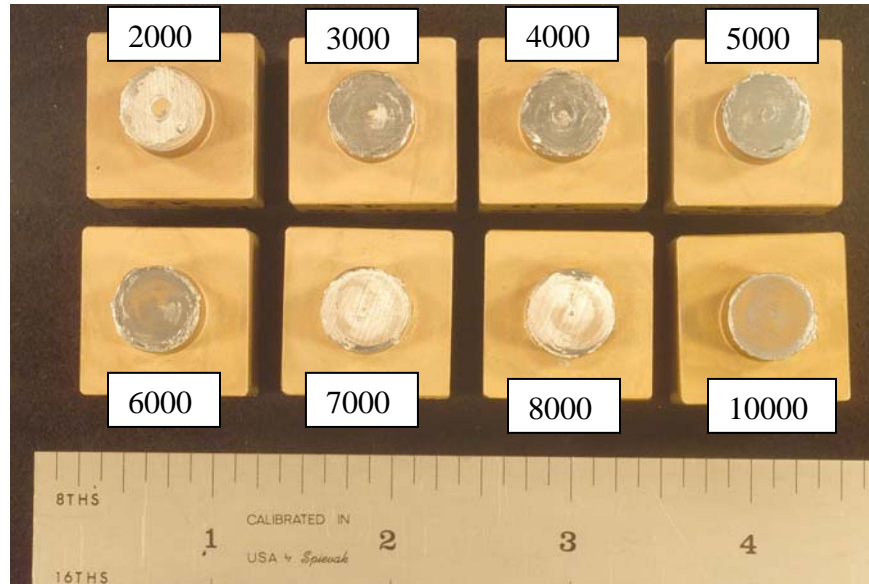
Figure 14. Cadmium plated steel buttons tested for galling on an AISI 4340 steel plate (see Figure 13), showing no galling at a maximum load of 10,000lbs.

The IVD aluminum coating was tested in the same manner as the cadmium plating. The testing was started at 2,000-lbs, and was raised by 2000-lbs until galling was noted. During testing it was noted that it was much more difficult to rotate the aluminum samples at low loads than the cadmium samples at higher loads. At 8,000-lbs, the aluminum-coated sample was unable to be rotated using two 8-inch lever arms. After approximately 1/8 (~45º) of a rotation, the test was stopped and the sample was removed and visually inspected. No galling was noted on the base metal, however it was assumed that the onset of cold welding was occurring and if the sample could have been rotated, metal would have been galled. A galling stress of 31 ksi was assumed for the IVD aluminum sample which are shown in Figures 15 and 16.
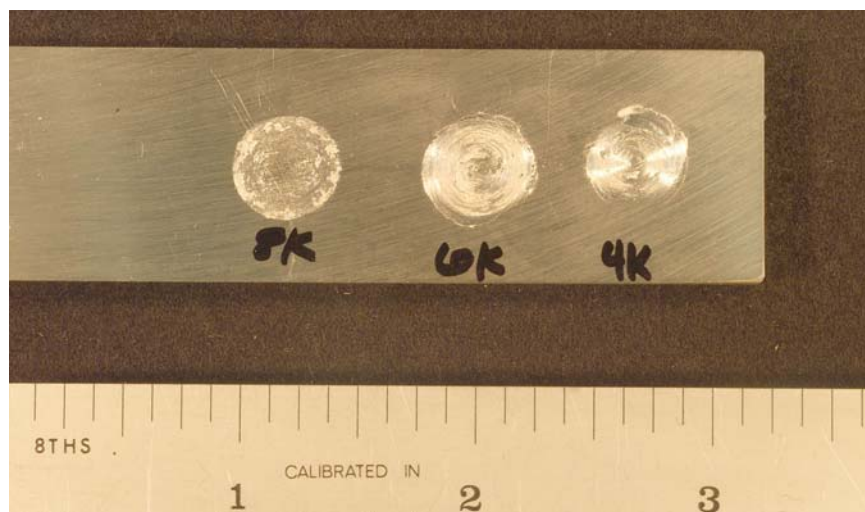

Figure 15. AISI 4340 steel plate tested for galling with IVD aluminum coated steel buttons, showing no obvious visible galling at a maximum load of 8,000-lbs.
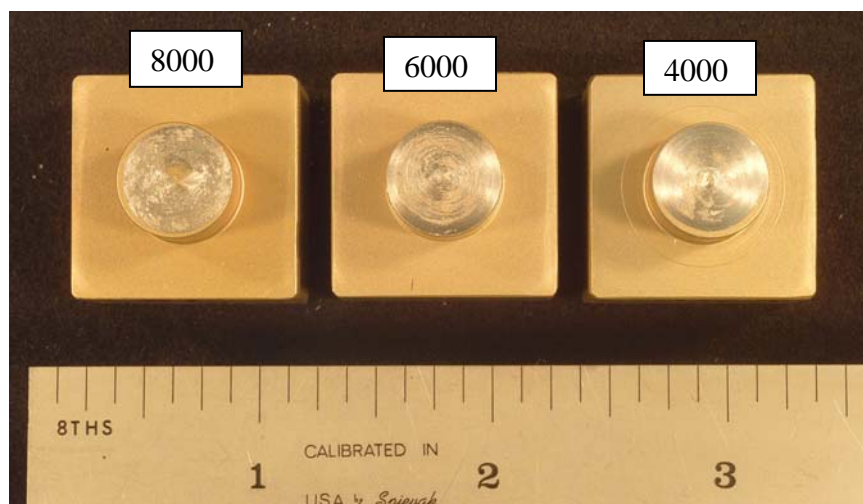
19

Figure 16.   IVD Aluminum coated steel buttons tested for galling on the AISI 4340 steel plate (see Figure15), showing no obvious visible galling at a maximum load of 8,000-lbs.

The P3PPA polymer coating was tested in the same manner as the cadmium plating. Separate rankings were done for the samples with and without the 2 μm graphite particles. The P3PPA samples, without graphite particles, were tested first. The test started at 2,000-lbs, where slight galling was noticed. The load was lowered to 1,000-lbs, where no galling was noted. The P3PAA coating was thin and uneven, making galling determination difficult. The coating did not seem to provide much protection against steel-to-steel contact. A galling stress of 10 ksi was assumed for the P3PPA samples without the graphite particles. The P3PPA graphite embedded samples were tested starting at 2,000-lbs, where no galling was noted, but nearly all of the polymer coating was smeared off of the button. The test operator noticed that there was not a noticeable increase in ease of rotation with the embedded graphite during testing. The load was increased to 4,000-lbs, where some slight galling of the base metal was observed. In order to determine the threshold galling stress of the sample, testing was performed at 3,000-lbs, where no galling was observed. Therefore, the threshold galling stress for P3PPA graphite embedded electroactive polymer is assumed to be approximately 20 ksi. Figures 17 and 18 show the results of the P3PPA samples with graphite embedded in the surface.
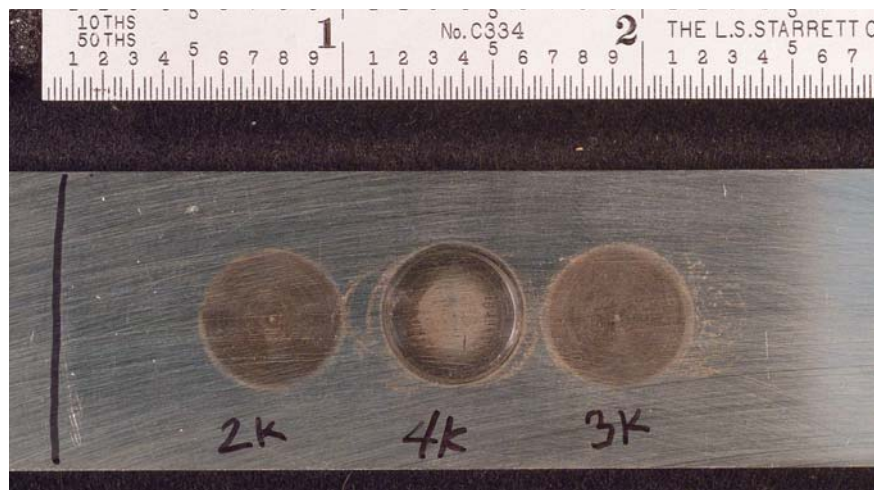
Figure 17. AISI 4340 plate tested for galling with electroactive polymer P3PPA coated buttons with embedded graphite, showing slight galling at a load of 4,000-lbs.
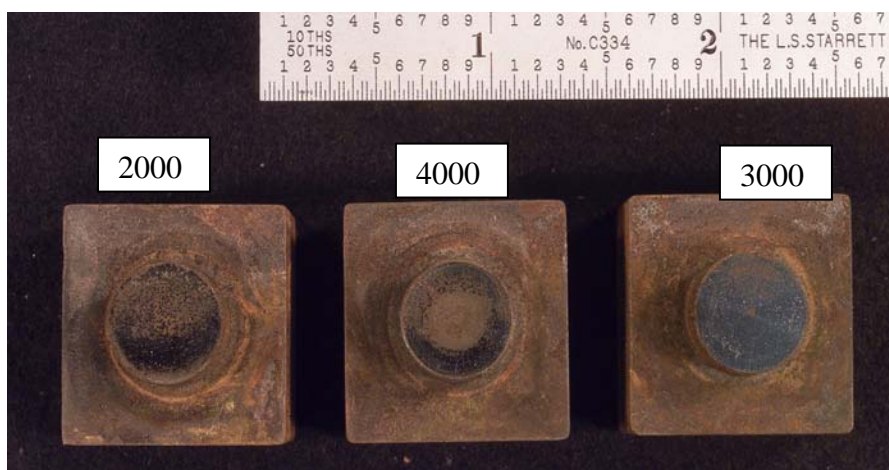

Figure 18. Electroactive polymer P3PPA coated buttons with embedded graphite tested on AISI 4340 plate (see Figure 17), showing slight galling at a load of 4,000-lbs.

The P3HT coating was tested starting at 4,000-lbs. It was noted that this coating behaved similarly to grease. The surface roughness of this coating could not be measured due to the poor adhesion of the coating. When the buttons were cleaned in isopropyl alcohol, the coating began to flake off, therefore the cleaning step was omitted for the remaining P3HT samples. The three remaining samples were tested at 4,000-lbs, 6,000-lbs, and 8,000-lbs, where no galling was noted on any of the samples.

Polymer sample P3PPAwas tested with both embedded MoS_2 and SiO_2 particles. The P3PPA MoS_2 samples were tested at 2,000 and 4,000-lbs. At 4,000-lbs galling of the coating was observed. The button and plate were fused together after testing and when they were broken apart, torn coating was seen. The P3PPA SiO_2 samples were tested in a similar manner, starting at 2,000-lbs. These samples were difficult to turn, showing poor lubricity, but no visible galling

was noted. At 8,000-lbs the samples were unable to turn, and a galling stress of 41 ksi was assumed. The results can be seen in Figures 19 and 20 show the samples with MoS_2 while Figures 21 and 22 show the samples with SiO_2.
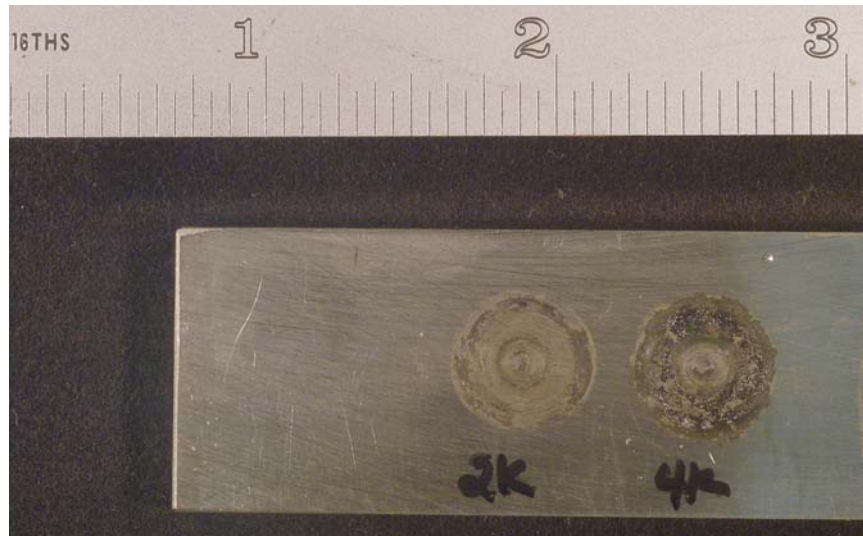

Figure 19.   AISI 4340 plate tested for galling with electroactive polymer P3PPA with MoS_2 coated buttons, galling of the coating was noted at a load of 4,000-lbs.
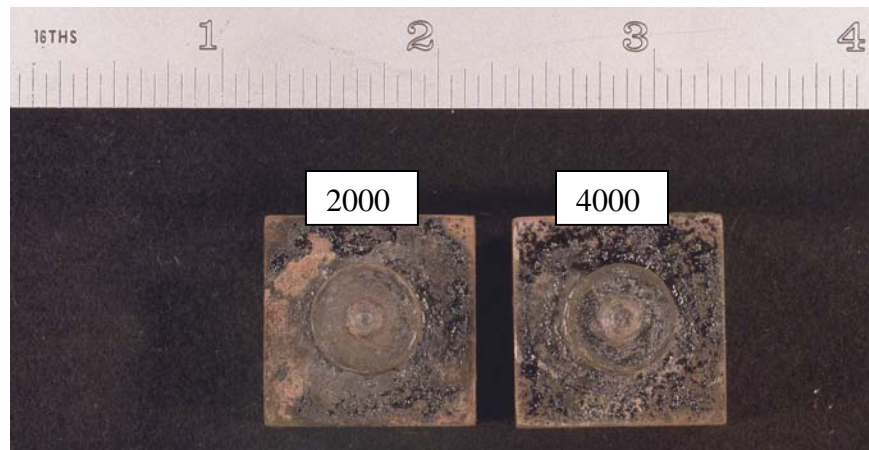

Figure 20.   Electroactive polymer P3PPA with MoS_2 coated buttons tested on AISI 4340 plate (see Figure 19), galling of the coating was noted at a load of 4,000-lbs.
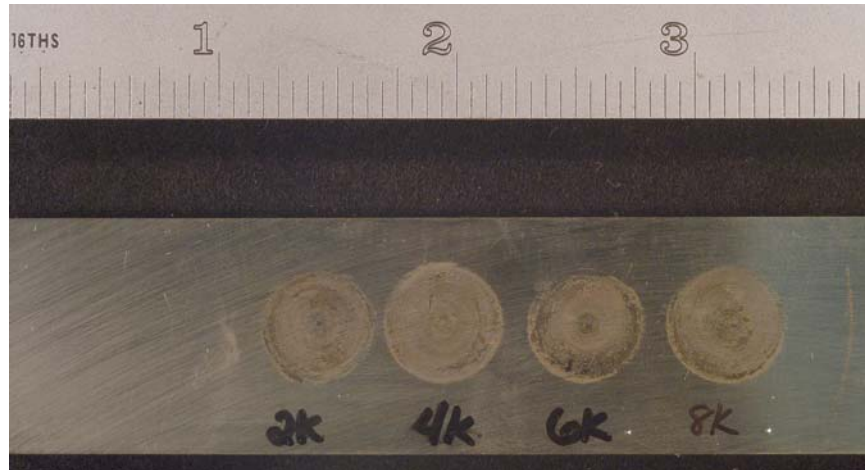
Figure 21: AISI 4340 plate tested for galling with electroactive polymer P3PPA + SiO$_2$ coated buttons, galling was assumes at 8,000-lbs when the button could no longer be rotated.
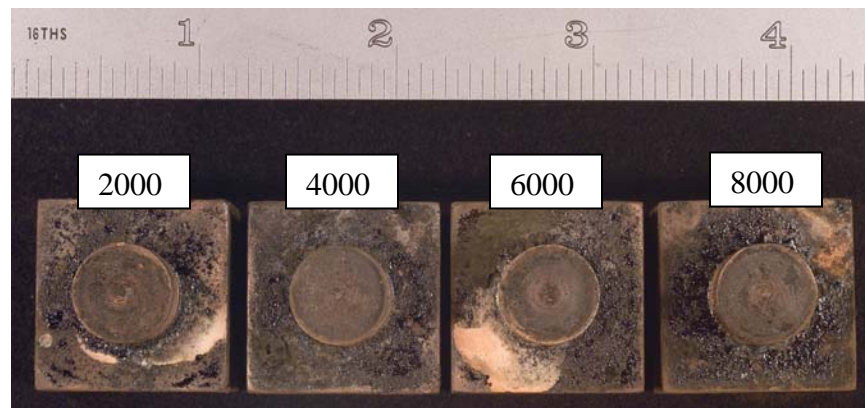

Figure 22. Electroactive polymer P3PPA with SiO$_2$ coated buttons tested on AISI 4340 plate (see Figure 21), galling was assumed at 8,000-lbs when the button could no longer be rotated.

Final samples of P3PPA with boron carbide were also tested for their galling resistance properties. The P3PPA was a very thin layer of coating, and showed little galling resistance over direct steel on steel contact. P3PPA showed some initial signs of galling at a load of 2,000-lbs.and with the addition of boron carbide to the P3PPA resulted in only a minimal increase in galling resistance. The coating flaked off during rotation and galling was noticed at a load of 4,000-lbs.

Scanning Electron Microscopy: ASTM G98 states that only the unaided eye shall be used to determine whether or not a system exhibited signs of galling. However, for the purpose of more thoroughly ranking coating galling resistance, a scanning electron microscope (SEM) was used to identify signs of galling at high magnification. Cadmium is a traditionally gall resistant

coating, and exhibited coating smearing accounting for its lubricity when examined under the SEM. Figure 23 shows the cadmium coating tested at 10,000-lbs at a magnification of 500x. IVD aluminum was also examined with the SEM for comparison purposes. Figure 24 shows the plate tested at 6,000-lbs, showing metal transfer and tearing of the aluminum coating. The various polymer coatings were examined with the SEM to see if the same desired metal smearing could be observed. Figure 25 shows a SEM image of coating P3PPA with SiO_2 on a button tested at 6,000-lbs. This samples shows metal smearing and some tearing, but the tearing seems to be less than IVD aluminum tearing at 6,000-lbs.
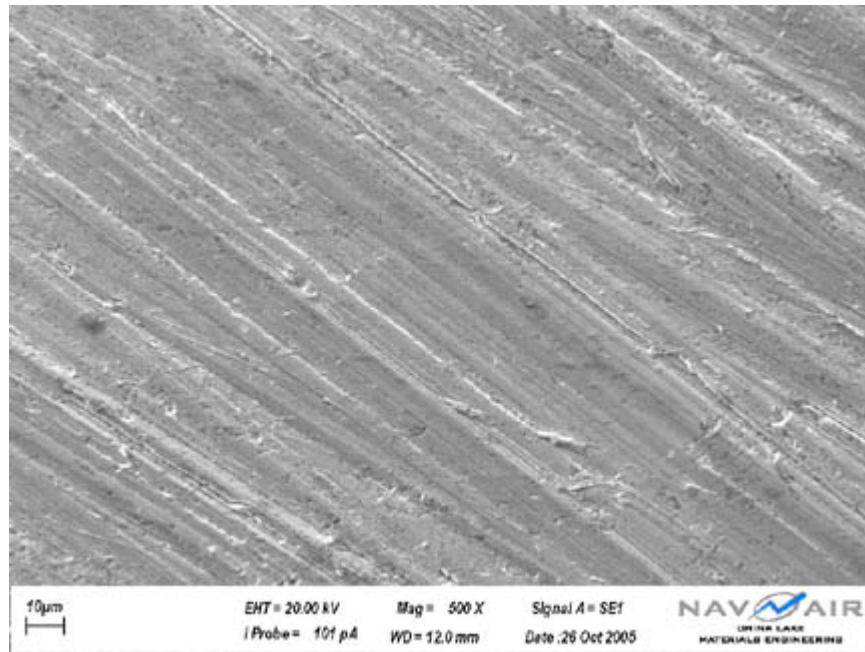
Figure 23.   Cadmium coated buttons tested on AISI 4340 plate at 10,000-lbs (51ksi). Coating smearing was noticed, but no evidence of coating or base metal galling. 500X.

Base steel

Coating transfer and smearing
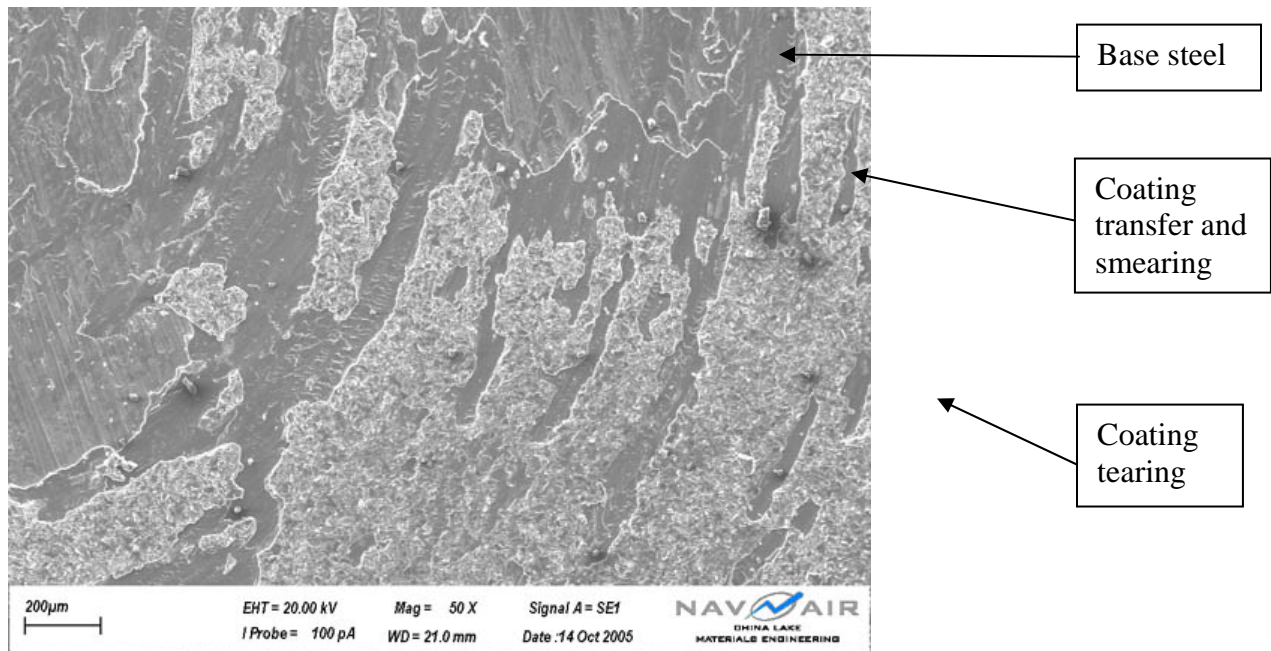
Coating tearing

Figure 24.   AISI 4340 plate galling tested for galling with IVD Aluminum coated button at 6,000-lbs. Coating transfer and tearing was noticed. 50X

Coating tearing

Figure 25.   P3PPA with SiO₂ button galling tested at 6,000-lbs, showing significant metal transfer, but less tearing that observed with the IVD aluminum. 100X

The results of the galling studies using the EAPs and micro-and nano-particles are summarized in Table 6 which shows the threshold galling stress of each of the tested coatings. The threshold galling stress is defined by ASTM G98 as the stress where galling is first observed with the unaided eye. The stress was determined by dividing the testing load by the button 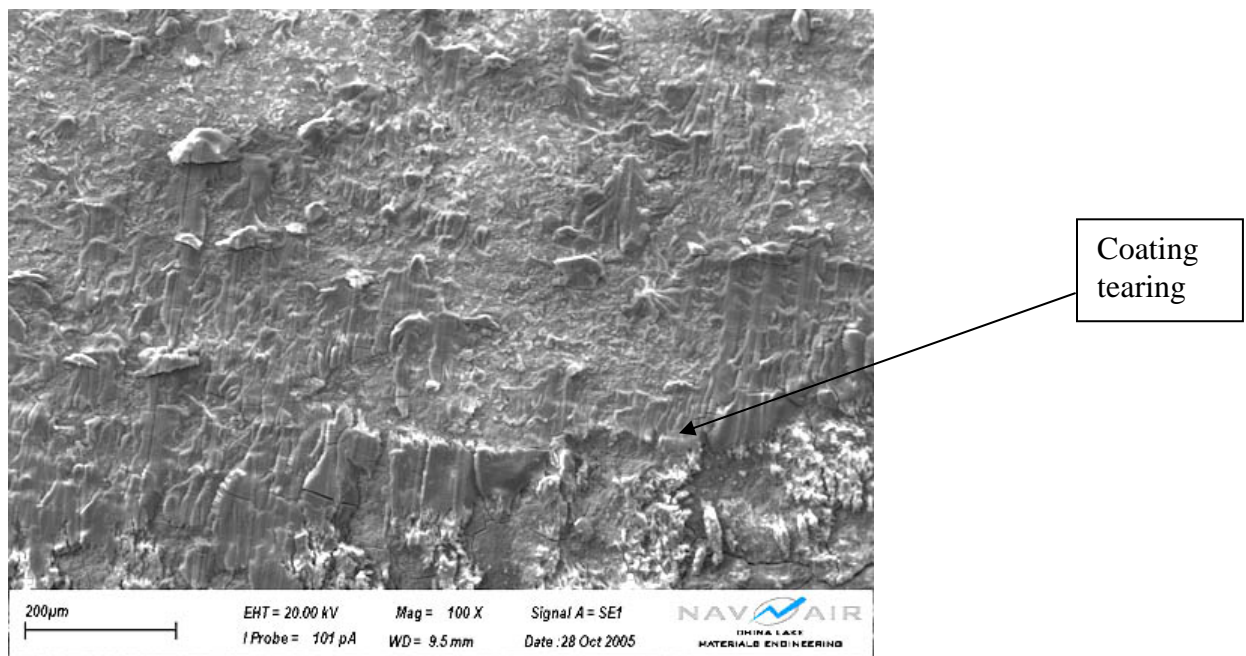area (.196 square inches). The table shows that cadmium exhibited the highest galling stress and the uncoated steel exhibited the lowest stress. Several of the polymer coatings provided little, if any, protection to steel on steel galling. Some of the other coating behaved more like a grease than a coating and did not provide an accurate galling resistance measurement. The P3PPA coating showed slight galling improvement with the addition of graphite particles. The P3PPA coating showed increased galling resistance with the addition of SiO_2, and seemed to show less galling than IVD aluminum.

Table 6. Threshold galling stress comparison of all tested coatings.

Coating	Maximum Testing Load (1000-lbs)	Threshold galling stress (ksi)	Comments
AISI 4340 steel - no coating	2	10	
Cadmium	10	>51	Maximum load
IVD Aluminum	6	31	Unable to move at 8klbs
P3PPA	2	10	Little protection over unprotected steel
P3PPA + graphite	4	20	No increase in lubricity noticed by operator
P3HT + MoS_2	8	>41	Low number of samples, coating acted like a grease
P3HT	8	41	Base metal galling, coating behaved like a grease
P3PPA + MoS_2	4	20	Coating galling
P3PPA+SiO_2	6	31	Unable to move at 8klbs
P3PPA	2	10 to 15	One sample only, very slight galling noted on metal
P3PPA + boron carbide	4	20	Coating flaked off, base metal galling

EIS Measurements and Neutral Salt Fog Tests: The spectra obtained for several days of exposure for Cd plated and P3PPA coated samples on high strength steel coupons (3x3x0.25) are given in Figures 26 and 27 respectively. The EIS spectra for the Cd plated high-strength steel reflect the corrosion behavior of metallic Cd in 0.5 N NaCl and can be fit to a simple one-time constant EC. The Cd metal surface was quite stable as evidenced by the more or less constant impedance spectra for exposure periods up to 8 days. E_{corr} also remained in a very narrow range. The spectra for the P3PPA coated steel samples resembled those for bare steel indicating that the coating did not provide corrosion protection (Figure 27). The E_{corr} values were close to those for bare steel. Rusting was observed on the exposed surfaces. The rusting is due to the pore film formation in which areas of the bare metal are not completely coated with the EAP. This same problem was observed in neutral salt fog exposure tests in which visible corrosion was evident in EAP samples (Figure 28). The neutral salt fog results are summarized in Table 7.
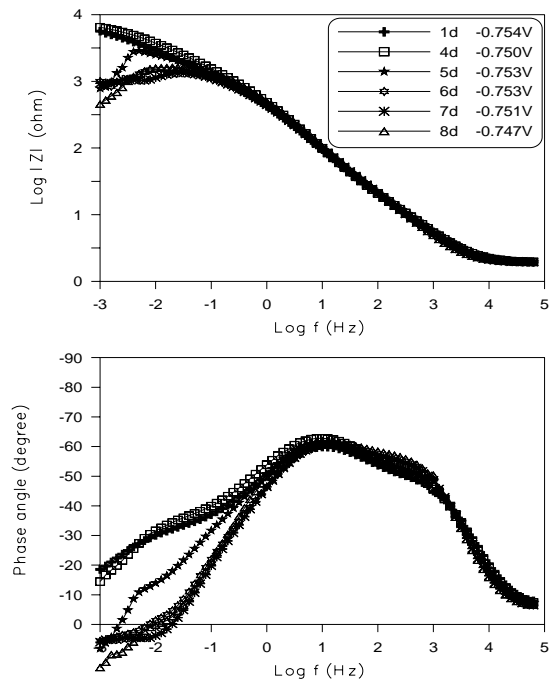
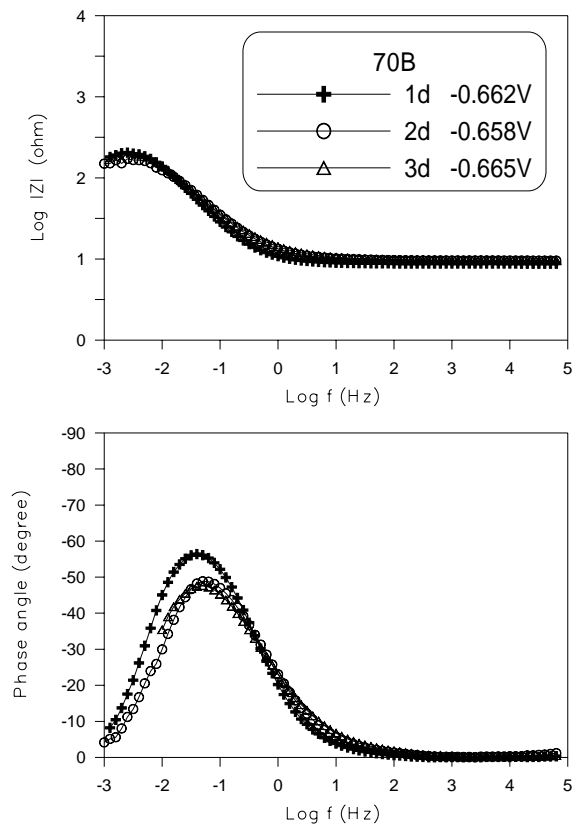**Figure 26.   Impedance spectrum of Cd plated high strength steel.**

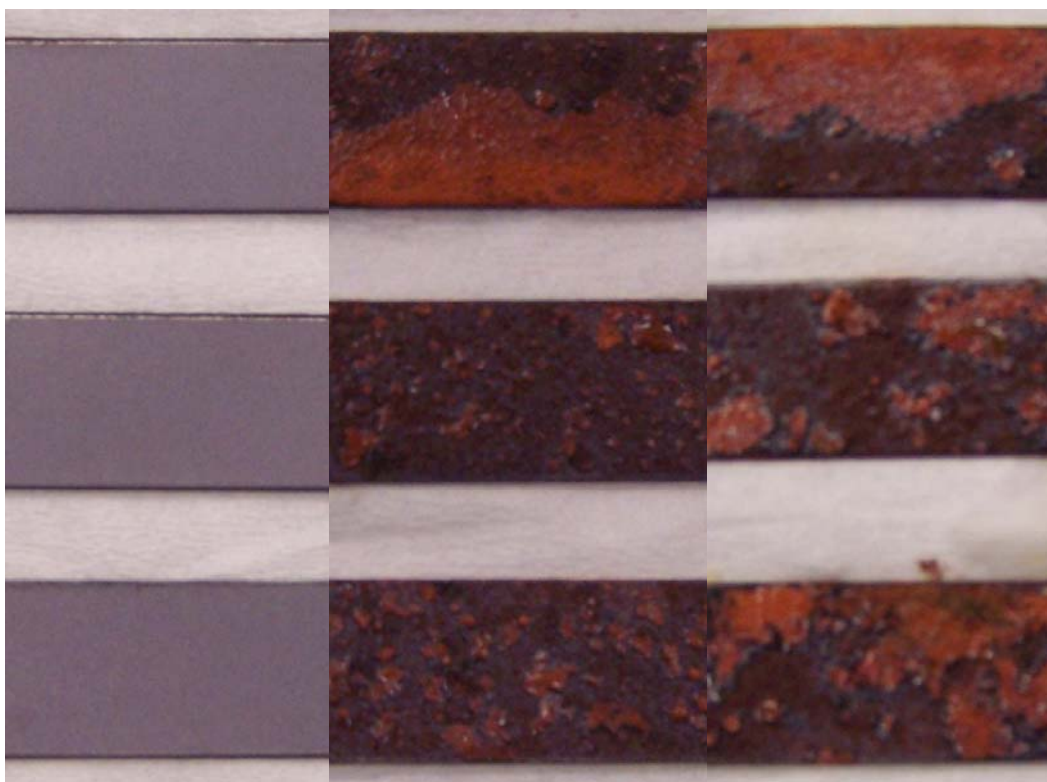**Figure 27.   Impedance spectrum of P3PPA coated high strength steel.**

Figure 28. Time = 0hrs (left), Time = 18hrs (middle), and Time = 42 hrs (right) for Neutral Salt Fog with Spray-cast TC + MoS$_2$ overcoat.

Table 7. Neutral Salt Fog Exposure Tests on 1008 and High Strength Steel Coupons.

EAP	Substrate	Application of Coating	Time (hrs) rust	Observation
Cd plated	High strength steel 4340	immersion	>96	No rust at 96 hrs
P3HT	1008	Spray	24	Rust localized to few spot on substrate
TP + MoS$_2$	1008	Spray	18	Rust
TC+ MoS$_2$	1008	Spray	18	Rust
P3PPA	High strength steel 4340	Electroless deposition	12	Rust

Discussion of Accomplishments and Future Work

In terms of the project goals, namely, synthesis of EAP-based materials and testing of the properties of interest, the work has shown some success. Although all of the improved properties have not been demonstrated simultaneously in a single material, the successful synthesis and testing has led to a greatly improved understanding of the key factors that influence the properties of interest. For instance, the corrosion testing clearly demonstrates that

the quality of the coating film and its adhesion to the substrate are the main determinant of corrosion resistance. The highest quality films resulted from the spray techniques used with the poly-alkylthiophenes, however, the best adhesion was observed in films made from polypyrrole (which had no alkyl side groups but a much higher concentration of acid groups) with a silane pretreatment. The latter films had flaking problems, which typically result from a glass transition temperature that is above room temperature, and can be solved by the use of alkyl-substituted pyrrole monomers. Both the chain length and concentration of acid groups could be systematically varied to produce an EAP with the optimal combination of properties. In addition, a combination of spray or powder coating, with a short electroless deposition to fill in any holes or inaccessible areas, could be used to optimize film quality. Since some corrosion protection from good quality EAP films is evident in the results, and since previously optimized EAP formulations have provided acceptable levels of corrosion protection in previously developed materials [25,26], there is good reason to believe that an optimized EAP, with the addition of hard particles to resist galling, would possess all the properties needed to serve as an effective replacement for cadmium-based coatings on high strength steels. In essence, the results have enabled us to identify the correct compositional elements, or pieces of the puzzle, for a successful coating system, what remains is to assemble and optimize the elements in order to produce a successful coating system.

Conclusions

The synthesis and characterization of novel polythiophenes and polypyrroles that can enable development of an EAP replacement for cadmium-based coatings on high strength steels has been accomplished. A combination of NMR, IR, and cyclic voltametry was used to confirm that these materials were produced and attached onto the steel surface. Application of the polymers onto steel substrates via air-brush and electroless deposition does not introduce toxic metals into the coated articles. The process has been shown to be an environmentally benign "green" alternative to the current use of Cd plating baths for high strength steel.

Several tests were performed on the EAP coated high strength steel specimens, with comparisons to Cd-based coatings and other alternative coating materials, in order to elucidate key structure-property relationships. Test results verified that no hydrogen embrittlement of the high strength steel samples results from using the electroless deposition process. Galling experiments showed that at least one EAP-based system containing a hard particle additive (embedded fumed silica) produced improved galling resistance when compared to IVD-Aluminum (though not cadmium), despite exhibiting limited lubricity. None of the EAP systems investigated provided corrosion protection comparable to cadmium-based coatings.

The corrosion protection ability of the films was strongly correlated to film quality, with defects due to flaking or pin-holes limiting the protective ability of the EAP-based systems. These issues are likely related to the chemical composition of the EAP materials, with insufficient alkyl substitution leading to flaking problems in the polypyrroles and insufficient acid group concentration leading to pin-holes in the polythiophene films. Thus, appropriate adjustment of the acid group and alkyl group concentrations should enable production of an EAP that would exhibit optimum film quality and acceptable corrosion protection.

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