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14. ABSTRACT The work in this report summarizes a four year, multi-disciplinary effort at North Dakota State University funded as a as a University Research Initiative grant that was part of a major funding program at AFOSR to address these needs. This study, entitled "Corrosion Testing, Lifetime Prediction, and Corrosion Sensor Development for Coated Aircraft Systems - Emphasis on Environmentally Compliant Practices," had as its goals the following: Improved Testing of Corrosion Protection of Coatings by ENM (electrochemical noise methods) and EIS (electrochemical impedance spectroscopy). Improved Lifetime Prediction of Coated Metal Systems Electrochemistry and SPM Microstructure Measurements at Metal/Polymer Interfaces, Development of New Data Analysis Methods, In-Situ Sensor Development Studies, and Improved Film Transport Property Characterization. The research team for this study was the interdisciplinary team of Prof. Gordon Bierwagen, Dept. of Polymers & Coatings, Prof. Dennis Tallman, Dept. of Chemistry, Prof. David Farden, Dept. of Electrical and Computer Engineering, and Prof. Marek Urban, Dept. of Polymers & Coatings. Prof. Urban left NDSU midway in the grant period and was replaced by Prof. Stuart Croll, Dept. of Polymers & Coatings.					
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Program Manager: Lt. Colonel Paul Trulove

Corrosion Testing, Lifetime Prediction, and Corrosion Sensor Development for Coated Aircraft Systems - Emphasis on Environmentally Compliant Practices

From: North Dakota State University
Fargo, ND 58105-5516

Principal Investigator: Prof. Gordon Bierwagen
Department of Polymers & Coatings

Co-PI's:
Prof. Dennis Tallman
Department of Chemistry

Prof. David Farden
Department of Electrical Engineering

Prof. Stuart Croll
Department of Polymers & Coatings

Prof. Marek W. Urban*
Department of Polymers & Coatings

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Chapter I

Executive Summary and Introduction

The current coatings system for the protection of US Air Force (AF) military aircraft are relatively high performance systems that unfortunately have as their basis for corrosion control the use of chromate-based metal pre-treatments (e.g., Alodine 1200 for Henkel Surface Technologies, Madison Heights, MI) and a strontium chromate pigmented spoxy-polyamide primer. The complete ban of chromates in coatings is imminent, and the current costs of hazardous materials handling (HAZMAT) from the depainting of such AF aircraft are a significant contribution to the circa \$800 million/year airfleet maintenance cost of the AF. Further, a genuinely significant increase in the protective lifetime of AF aircraft coatings would yield an equally significant reduction in these same maintenance costs by considerably reducing the frequency of Depot Maintenance visits by these aircraft.

To further compound the situation, the function of the Cr^{+6} in the Al alloy pretreatment and in the currently used inhibiting primer is neither clearly understood nor well characterized, making replacement with environmentally acceptable materials very difficult. New test procedures for corrosion protective performance and lifetime prediction of USAF coating systems are also needed, as currently specified USAF tests for coating performance are unacceptable because of their subjective nature and lack of accuracy and they are very time consuming. Further, the USAF would like sensors to insert under coated metal parts to assess current status *vis a vis* corrosion protection and remaining lifetime of these parts.

Thus, research work was needed to support the AF efforts to develop extended lifetime, chromate free coatings systems for its airfleet. The work in this report summarizes a four year, multi-disciplinary effort at North Dakota State University funded as a as a University Research Initiative grant that was part of a major funding program at AFOSR to address these needs. This study, entitled "Corrosion Testing, Lifetime Prediction, and Corrosion Sensor Development for Coated Aircraft Systems – Emphasis on Environmentally Compliant Practices," had as its goals the following:

- Improved Testing of Corrosion Protection of Coatings by ENM (electrochemical noise methods) and EIS (electrochemical impedance spectroscopy),
- Improved Lifetime Prediction of Coated Metal Systems
- Electrochemistry and SPM Microstructure Measurements at Metal/Polymer Interfaces,
- Development of New Data Analysis Methods,
- In-Situ Sensor Development Studies, and
- Improved Film Transport Property Characterization.

The research team for this study was the interdisciplinary team of Prof. Gordon Bierwagen, Dept. of Polymers & Coatings, Prof. Dennis Tallman, Dept. of Chemistry, Prof. David Farden, Dept. of Electrical and Computer Engineering, and Prof. Marek Urban, Dept. of Polymers & Coatings. Prof. Urban left NDSU midway in the grant period and was replaced by Prof. Stuart Croll, Dept. of Polymers & Coatings.

As described in this report and others resulting from this grant, significant success was achieved in meeting the goals of this study. An improved cyclic test protocol, based on ASTM 5894-96, was examined for its viability with respect to aircraft coatings systems, and then introduced as the NDSU protocol for such testing throughout the entire project. This test protocol has the following attributes:

- Simulates effects of sunlight with UV lamps
- Simulates effects of dew and rain with water condensation and salt spray
- Accelerates corrosive effects by elevating test temperature
- A cyclic test: combination of sunlight, electrolyte, and thermal effects
- Past study has shown that resultant relative corrosion rates, structure, and morphology similar to those seen outdoors
- Protocol (ASTM D 5894-96) has been previously and successfully used in testing of automotive coatings - similar materials & similar exposure issues.

The effects of this test protocol on standard AF coatings on Al 2024 T-3 were examined by an extensive set of characterization methods including the electrochemical methods ENM and EIS, AFM, microscopic FTIR, spot Raman and FTIR-PAS spectroscopic methods, gloss, color and contact angle measurements. Our EIS and ENM studies have yielded a lifetime prediction methodology for the corrosion protective properties of the coating systems under study. The accuracy and methodology for routine ENM and EIS measurements for the characterization of the corrosion protective properties of aircraft coatings systems has been considerably enhanced, and new spectral methods for examining ENM data have been developed. The methodology is being extended to newer AF coatings systems and experimental coatings systems. Further, the effects of UV radiation on the polyurethane systems presently in use by the AF have been analyzed in a quantitative way by advanced micro-spectroscopic methods, and quantitative descriptions of this mode of degradation are emerging.

During the course of this work, NDSU became involved in the consideration of coatings based on doped conductive polymers as a chromate-free primer coating to consider as possible replacements for the present (pretreatment + primer coating) usage based on chromates. We have considered doped polyaniline materials for Monsato (PANDATM) and other conductive polymers such as poly(alkyl-pyrrole)s. One of the conductive polymer primer films based on poly(3-octylpyrrole) topcoated with a standard AF urethane topcoat has gone for > two years in immersion without showing significant visual failure. In these studies, which have generated several potential candidate Cr replacement materials, we have introduced the use of the scanning vibrating electrode technique (SVET), developed by H. Isaacs at Brookhaven Labs, to measure the "damage protection" mechanism of first, the present chromate systems, and then the conductive polymers. The SVET measurements have become a standard technique in our lab for quantifying the damage protection properties of systems, especially with reference to existing chromated systems.

We have also developed new equipment and methods for performing both EIS and ENM measurements. We have developed methods of creating "colored noise" that generates a test signal of chosen frequency, amplitude and phase angle that allows improved speed and accuracy in EIS studies. Proto-type systems based on DSP chips and methods are in the final stages of construction. Preliminary electrochemical measurements made with early, crude versions of this

instrumentation have shown feasibility of the method and instrumental design to perform accurate EIS measurements of coatings systems over Al 2024 T-3 substrates

Toward the end of the grant period, we also succeeded in demonstrating successfully *in situ* measurement of coating electrochemical properties by modified ENM measurements using two implanted Pt-wire electrodes over an Al 2024 T-3 substrate that was exposed in a corrosion test chamber using the Prohesion™ exposure test cycle. We were able to monitor changes in R_n , the noise resistance of the coating film as the film underwent temperature and electrolyte concentration variations. This system will be evaluated for its feasibility as an on-board corrosion sensor in field use in future studies.

Finally, we have shown that a chromate-free corrosion protection system based on an Mg-rich primer + the Extended -Life fluoropolymer/urethane topcoat originally formulated for the C-17 has > 3000 hours durability on a scribed sample in Prohesion cycle exposure. The Mg-rich coating, which is a modified epoxy based particulate Mg pigmented primer, provides cathodic protection for Al in a manner analogous to the cathodic protection Zn-rich primers provide to steel substrates. This system needs some optimization, but shows the potential for being a near-term solution for the chromate replacement problem.

Thus, most of the goals of the original proposal have been met, and this NDSU research team is now working on extensions of these studies, also under the support of AFOSR. These future studies are described in brief at the end of this report.

The structure of this report is that abstracts of reports and publications resulting from this research grant are presented under the individual PI and co-PI's headings. A bibliography of the publications and presentations prepared with full or partial support of this grant is given under each investigator as are the graduate students and post-doctoral research associates trained in this program as well as the graduate degrees granted for research done under this grant. Future extensions of these studies are described at the end of the report.

Chapter II

Contribution of Prof. Gordon Bierwagen Department of Polymers & Coatings

Summary of Research Activities and Results FY 1997 through FY 2000

Major Accomplishments:

Detailed in section below.

Equipment Additions:

Q-Fog cyclic corrosion testers (2), Q-Panel Lab Products

Various electrochemical instruments and software, Gamry Instruments

Constact angle/Surface energy analyzer, First Ten Angstrom

Micro-TA 2990 w/ Controller, TA Instruments

Wide Dynamic Range Optical Particle Sizer, Particle Sizing Systems

Computers/Electronics. Multiple computers and small electronics have also been added.

Personnel Contributing to this Study:

Youngun Pae, Dr. Sebastien Touzain, Seva Balbyshev, Junping Li, , Dr. Moussa Zoiudone, and Xianping Wang, Michael Nanna, Lingyun He, and Lisa Ellingson

Publications:

1. Gordon P. Bierwagen and Dennis E. Tallman, "Choice and Measurement of Crucial Aerospace Coating System Properties," **Prog. Organic Coatings**, **41** (2001) 201-217
2. Joseph H. Osborne, Kay Y. Blohowiak, S. Ray Taylor, Chad Hunter, Gordon P. Bierwagen, Brenden Carslon, Dan Bernard, and Michael S. Donley, "Testing and Evalation of Non-Chromated Coating Systems for Aerospace Applications," **Prog. Organic Coatings**, **41** (2001) 217-225
3. X.F.Yang, D.E.Tallman, V.J.Gelling, G.P.Bierwagen, L.S.Kasten & J.Berg, "Use of a Sol-Gel Conversion Coating for Aluminum Corrosion Protection," **Surface & Coatings Tech.**, **140** (2001) 44-50
4. Gordon Bierwagen, "The Next Generation of Aircraft Coatings Systems," *Proceeding of the XXVth FATIPEC Congress*, Turin, Italy, September 19-23, 2000, Vol. I, pp. 1-21, also as: Gordon Bierwagen, "The Next Generation of Aircraft Coatings Systems," **J. Coatings Tech.**, **73**(#915) (2001) 45.

5. H.K.Yasuda, C.M.Reddy, Q.S.Yu, J. Deffeyes, G.P.Bierwagen & L.He, "Effect of Scribing on Corrosion Test Results," **Corrosion**, **57**, (2001) 29-34
6. Gordon Bierwagen, Junping Li, Lingyun He, and Dennis Tallman "Fundamentals of the Measurement of Corrosion Protection and the Prediction of Its Lifetime in Coatings," accepted for publication in *Proceedings of the 2nd International Symposium on Service Life Prediction Methodology and Metrologies*, Monterey, CA, Nov. 14-17, 1999, J. Martin and D Bauer, ed., ACS Books, Washington, DC (est. publ. Fall 2001)
7. K.D.Conners, W.J.Van Ooij, D.J.Mills, G.P.Bierwagen, "Comparison of Electrical Impedance Spectroscopy and Electrochemical Noise Measurement of Plasma Polymerized Films as pretreatment for ColdRolled Steel," **British Corrosion J.**, **35** (2000) 141-144
8. Gordon P. Bierwagen*, J. Li, L. He & L. Ellingson & D.E.Tallman, "Consideration of a New Accelerated Evaluation Method for Coating Corrosion Resistance – Thermal Cycling Testing," **Prog. Organic Coatings**, **39** (2000) 67-78
9. R.L.De Rosa, J.T.Grant, L. Kasten, M. Donley, & G.P.Bierwagen, "Surface Analysis of Various Methods of Preparing Al 2024 T-3 Surface for Painting," **Corrosion**, **56** (2000) 395-400
10. Gordon Bierwagen, D.E.Tallman, J. Li, S. Balbyshev, & M. Zuidone, "Electrochemical Noise Studies of Aircraft Coatings over Al 2024 T-3 in Accelerated Exposure Testing," Refereed Paper 00427, CORROSION 2000, NACE Annual meeting, Orlando, FA, March 26-31, 2000
11. Jie He, Victoria Johnston Gelling, Dennis E. Tallman, and Gordon P. Bierwagen, "A Scanning Vibrating Electrode Study of Chromated-Epoxy Primer on Steel and Aluminum," *J. Electrochem. Soc.*, **147**(2000) 3661-3666
12. Jie He, Victoria Johnston Gelling, Dennis E. Tallman, Gordon P. Bierwagen and Gordon G. Wallace, "Conducting Polymers and Corrosion III: A Scanning Vibrating Electrode Study of Poly(3-Octyl Pyrrole) on Steel and Aluminum," **J. Electrochem. Soc.**, **147** (2000) 3667-3672
13. G.P.Bierwagen, J. Li, N. Davis, & D. E. Tallman, "Thickness Dependence of Electrochemical Properties of Organic Coatings," *Proc. 5th Nuernberg Congress*, Vol. 1, p.315, Nuernberg, Germany, April 12-14, 1999, Vincentz Verlag, Hannover, Germany (non-refereed)
14. D.E.Tallman, Y. Pae, & G.P.Bierwagen, "Conducting Polymers and Corrosion 2: Polyaniline on Aluminum Alloys," **Corrosion**, **56** (2000) 401-410
15. D.E.Tallman, Y. Pae, & G.P.Bierwagen, "Conducting Polymers and Corrosion: Poly(aniline) on Steel," **Corrosion**, **55** (1999) 779
16. G.P.Bierwagen, R.S.Fishman, T. Storsved, & J. Johnson, "Recent Studies of Particle Packing in Organic Coatings," **Prog. Organic Coatings**, **35**(1999) 1-10

17. G.P. Bierwagen, D.E.Tallman, S. Touzain, A. Smith, R. Twite V. Balbyshev & Y. Pae, "Electrochemical Noise Methods Applied to the Study of Organic Coatings and Pretreatment," *Paper 380, Corrosion 98*, Reviewed paper for the 1998 Annual Meeting of the Nat. Assoc. Corrosion Eng. (NACE), NACE Int., San Diego, CA, March 1998
18. G.P.Bierwagen, "Corrosion and Its Control by Organic Coatings," Ch. 1 in American Chemical Society, ACS Symposium Series **689**, *Organic Coatings for Corrosion Control*, G.P. Bierwagen, ed. 1998, p. 1
19. Vsevolod N. Balbyshev, Gordon P. Bierwagen & R.L. Berg "Electrochemical Studies of Vinyl Ester Coatings for Fuel Tanks," Ch. 23 in American Chemical Society, ACS Symposium Series **689**, *Organic Coatings for Corrosion Control*, G.P. Bierwagen, ed. 1998, p292
20. U.G. Hermann, G. P. Bierwagen D.J. Mills V. H. Hauser "Electrochemical Properties of Coatings from Renewable Natural Products," Ch. 35 American Chemical Society, ACS Symposium Series **689**, *Organic Coatings for Corrosion Control*, G.P. Bierwagen, ed1998, p.423
21. Carol S. Jeffcoate, Gordon P. Bierwagen "Electrochemical Comparison of Coating Performance in Flowing vs. Stationary Electrolyte" Ch. 12 in American Chemical Society, ACS Symposium Series **689**, *Organic Coatings for Corrosion Control*, G.P. Bierwagen, ed1998, p.151
22. Rebecca L. Twite & Gordon P. Bierwagen, "Calculation of Defect Area Under a Coating Using Electrochemical Analysis," Ch. 25 in American Chemical Society, ACS Symposium Series **689**, *Organic Coatings for Corrosion Control*, G.P. Bierwagen, ed. 1998, p.308
23. Gordon P. Bierwagen, D.E.Tallman, C. S. Jeffcoate, & J. Zlotnick "Defects & Heterogeneities in Corrosion Protective Organic Coatings Films and Their Effects on Performance," Ch. 10 in American Chemical Society, ACS Symposium Series **689**, *Organic Coatings for Corrosion Control*, G.P. Bierwagen, ed1998, p.123
24. R.L.Twite, G.P.Bierwagen, "Review of Alternatives to Chromate for Corrosion Protection of Aluminum Aerospace Alloys," **Prog. Org. Coatings**, **33** (1998) 91-100
25. J.Li, C.S.Jeffcoate, G.P.,Biewagen, D.J.Mills & D.E.Tallman, "Thermal Transition Effects and Electrochemical Properties in Organic Coatings: I. Initial Studies on Corrosion Protective Organic Coatings," **Corrosion**, **54** (1998) 763-771
26. C.S.Jeffcoate, T.L.Wocken, and G.P.Bierwagen, "Electrochemical Assessment of Spray-Applied Thermoplastic Coating Barrier Properties," **J. Materials Eng. & Performance**, **6** (1997) 417-420
27. L.B.Reynolds, R.Twite, M.S.Donley, G.P.Bierwagen & M. Khobaib, " Preliminary Evaluation of the Anticorrosive Properties of Aircraft Coatings by Electrochemical

Methods," **Prog. Organic Coatings**, **32** (1997) 31-34

28. G.P.Bierwagen, R.Twite, G.Chen, & D.E.Tallman, "AFM,SEM and Electrochemical Characterization of Al Alloys Conversion Coatings, and Primers used for Aircraft," **Prog. Organic Coatings**, **32**(1997) 25-30

Presented Papers & Project Reports:

(Non-Refereed) *= presenter if not GPB

Gordon Bierwagen, "EIS Studies of Coated Metal in Accelerated Exposure, "Invited Keynote Speaker, EIS 2001, Marilleva-Trento, Italy, June 17-22, 2001

Xianping Wang, Gordon Bierwagen, & Dennis Tallman, "Embedded Electrodes for *In Situ* ENM Measurements," Presented at The Second International Workshop "Application of Electrochemical Techniques to Organic Coatings," Jurata Poland, May 14-17, 2001

Xianping Wang, Gordon Bierwagen, & Dennis Tallman, "Use of Electrochemical Noise Methods (ENM) for *In Situ* Monitoring of Coatings Electrochemical Properties During Accelerated Exposure Testing," Paper 178 Presented at the 199th Meeting of The Electrochemical Society, Washington, DC, March 25-30, 2001

Gordon Bierwagen, "Chromate-Free Corrosion Protective Coatings Systems for Al Alloy 2024-T3," Invited Lecture at Aluminum Chair 2001 – Aluminum in the Aerospace Industries, Gosselies, Belgium, March 22, 2001

Gordon Bierwagen, "Past and Present Development of the CPVC Concept and Its Applications to Coatings Design and Formulation," Invited Presentation to the Philadelphia Society for Coatings Technology, March 1, 2001

Gordon Bierwagen, "The Next Generation of Aircraft Coatings Systems," Invited Plenary Lecture, XXVth FATIPEC 2000 Congress, Turin, Italy, September 19-23, 2000

Gordon Bierwagen, "A Review of the Critical Pigment Volume Concentration and Particle Packing Effects in Organic Coatings and Filled Polymers, " Invited one day training session for technical personnel at Rohm & Haas Research Laboratories, Springhouse, PA, June 2, 2000

Gordon Bierwagen, "Environmentally Benign Corrosion Protection by Coatings for Steel and Al Alloys: Present and Future," Invited Lecture, Great Lakes Regional Meeting, American Chemical Society, Fargo, ND June 4, 2000 Paper 121

Moussa Zidoune, Gordon Bierwagen, Junping Li and Dennis Tallman, "Characterization of Aircraft Coatings by Electrochemical Impedance Spectroscopy," Paper # 1290, Presented at the 197th Meeting of the Electrochemical Society, Toronto, Canada, May 14-18, 2000

Lingyun He*, Gordon Bierwagen, & Dennis Tallman, " A Rapid Corrosion Resistance Test Protocol for Organic Coatings System: Thermal Cycling + Impedance Measurements," Paper 1296, Presented as a Poster at the 197th Meeting of the Electrochemical Society, Toronto, Canada, May 14-18, 2000

Xianping Wang*, Gordon Bierwagen & Dennis Tallman, "Electrode Configurations for *In situ* Electrochemical Impedance Measurements on Coated Metal Systems," Paper 1297, Presented as a Poster at the 197th Meeting of the Electrochemical Society, Toronto, Canada, May 14-18, 2000

Gordon Bierwagen, D.E.Tallman, J. Li, S. Balbyshev, & M. Zuidone, "Electrochemical Noise Studies of Aircraft Coatings over Al 2024 T-3 in Accelerated Exposure Testing," presented at CORROSION 2000, NACE Annual meeting, Orlando, FA, March 26-31, 2000

Gordon Bierwagen, "Corrosion Protective Coatings for the New Millennium," Invited Plenary Presentation for the Kansas City Society for Coatings Technology Annual Symposium, March 14, 2000, Kansas City, MO

Gordon Bierwagen, "Chromate Replacement in the Protection of Steel and Aluminum Alloys," Invited presentation at the 8th Forum de la Connaissance, sponsored by the AFTPV (Assoc. Francaise des Techniciens des Peintures et Vernis) and CoRI (Coatings Research Institute, Limlette, Belgium), Paris, France, December 1-2, 1999

Gordon Bierwagen, "Fundamentals of Corrosion and Corrosion Protection," invited presentation at the 2nd International Symposium on Service Life Prediction Methodology and Metrologies, sponsored by NIST, NSF, NREL, AFRL -WPAFB, FHWA, and USDA - FPL, Madison, Monterey, CA, Nov. 14-17, 1999

Gordon Bierwagen, Seva Balbyshev, Junping Li and Dennis Tallman,* "Comparison of Electrochemical Noise Data to Electrochemical Impedance Spectroscopy Data for Organic Coatings on Metals," presented at the 196th National Meeting of The Electrochemical Society, Honolulu, Hawaii, Oct. 17-22, 1999

Gordon P. Bierwagen*, J. Li, & D.E.Tallman (*presenter), "Electrochemical Measurements and Lifetime Predictions for Organic Coating/Metal Systems," invited presentation at the Symposium on Long - Lived Aircraft Primers, Air Force Research Laboratory, WPAFB, Ohio, July 28-29, 1999

Gordon Bierwagen, Joel Johnson, & Michael Nanna, "Current Developments in Making Organic Coatings Formulation a Science: Coating Design," Invited presentation, 1999 Gordon Research Conference on Coatings & Films, July 11-16, 1999, New London, NH

Gordon P. Bierwagen*, J. Li, L. He & L. Ellingson (*presenter) & D.E.Tallman, "Consideration of a New Accelerated Evaluation Method for Coating Corrosion Resistance - Thermal Cycling Testing," International Workshop, "Application of Electrochemical Techniques to Organic Coatings," 6- 9 May 1999, Schliffkopf Hotel, Black Forest, Germany,

Gordon Bierwagen*, Junping Li, Newton Davis, and Dennis Tallman, "Thickness Dependence of Electrochemical Properties of Organic Coatings," Invited Presentation, 5th Nurnberg Congress - Creative Advances in Coatings Technology, Nürnberg, Germany, April 12-14, 1999

A.Donescu, Q.Le Thu, S. Touzain,* & G. P.Bierwagen, "EIS and ENM Measurements for Three

Different Polymeric Systems on Aluminum," Presented at the 11th Forum sur les Impedances Electrochimiques, 18 December 1998, Paris. Organized by C. Garielli, UPR 15 Physique de Liquides et Electrochimie, CNRS, Université Pierre et Marie Curie, Paris

G. Bierwagen, "An Examination of Transport Properties of Organic Coatings As Related to Corrosion Prevention," Invited Presentation, 5th Biennial Conference on the Science and Technology of Organic Coatings, Nov. 8-11, 1998, Hilton Head, SC

Gordon Bierwagen "Corrosion Testing and Lifetime Prediction" Presented at the DARPA/AFOSR Coatings and Corrosion Program Review, September 28-30, 1998, Annapolis, MD.

G.P. Bierwagen, H.Yasuda, R. Twite, J. Li*, L.He, L. Ellingsen, D. Tallman, "Investigation of Chromate-free Plasma-Polymer Based Coatings for Aircraft Alloys," presented on Aug. 26, 1998 at the 3rd Int. Aircraft Corrosion Workshop, Solomons Is., MD, sponsored by ONR and NASC, hosted by NAWC

Gordon P. Bierwagen, Dennis E. Tallman, Marek W. Urban, "Choice and Measurement of Crucial Aerospace System Properties," invited presentation, Workshop on Advanced Metal Finishing for Aerospace Applications, Keystone, CO, Aug. 23-28, 1998, sponsored by Air Force Research Laboratory, Materials & Mfg. Directorate, WPAFB, OH

D.E.Tallman*, Y. Pae, G. Chen, G.P.Bierwagen, B. Reems & V. Gelling, "Studies of Electronically Conducting Polymers for Corrosion Inhibition of Aluminum and Steel," invited presentation at ANTEC (Annual Technical Conference of the Society of Plastics Engineers) Atlanta, GA, April 27-30, 1998

G.P. Bierwagen, D.E.Tallman, S. Touzain, A. Smith, R. Twite V. Balbyshev & Y. Pae, "Electrochemical Noise Methods Applied to the Study of Organic Coatings and Pretreatment," *Paper 380, Corrosion 98*, presented at the 1998 Annual Meeting of the Nat. Assoc. Corrosion Eng. (NACE), NACE Int., Houston TX, March 1998

G.P.Bierwagen C.Jeffcoate, N. Davis and Sebastien Touzain, "Initial Studies of Electrochemical Comparison of Coating Performance in Flowing vs Stationary Electrolyte," presented at the Tri-Service Corrosion Conference, Wrightsville Beach, NC, Nov. 17-21, 1997

G.P.Bierwagen, "Observations on Electrochemical Noise Methods (ENM) to Study Coated Metals," Presented at the International Symposium on ADVANCES IN CORROSION PROTECTION BY ORGANIC COATINGS (ACPOC), Oct. 29-31, 1997, Science University of Tokyo, Noda, Japan

G.P. Bierwagen, "Recent Studies of Particle Packing in Organic Coatings," Invited Lecture at the 70th Anniversary Conference on Colour Materials, Japan Society of Colour Materials, Tokyo, Japan, Oct. 22-24, 1997

G.P. Bierwagen, "Electrochemical Noise for the Testing of Coatings," Presented at the Twin

Cities Section of the Electrochemical Society, Minneapolis, MN May 15 1997

G.P.Bierwagen, J. Li, C.S.Jeffcoate, and N. Davis, "Film Resistivity of Organic Coatings - Characterization and Use," Presented at Corrosion 97, Research in Progress Symposium,, NACE Annual Meeting, New Orleans, March 11, 1997

Graduate Theses:

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Initial Coatings Studies

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Major Hugh De Long, Program Manager

We are performing studies on coatings film thickness effects on electrochemical behavior of coatings. Our work for this project has mainly concentrated on the analysis of data from this experimental study, and ways of improving the data analysis of the time series data we are acquiring as $R_n(t)$ and $|Z(t)|$. This data is being examined for trends and decay rates. We are also examining some polyaniline films as coatings. The polyaniline was acquired in the doped form from Monsanto, and examined originally over steel in 3% NaCl. We are currently examining it over Al alloys. The work on coatings is emphasizing the following:

Testing of Corrosion Protection of Coatings

1. ENM & EIS Studies
2. Electrochemical Testing in conjunction with exposure testing
3. Adhesion Testing in conjunction with exposure testing
- Various Exposure Methods and Measurements plus Electrochemical Testing
5. Studies on imperfect & damaged systems
6. Chromate Pretreatment & Chromate-Based Pigments in Testing
7. Statistical Validation of Corrosion Test Data
8. Development of New Analysis Software for ENM & EIS
9. Coating Ranking Procedures

Improvements in Exposure Testing of Samples in ENM and EIS

Presented in
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Major Hugh De Long, Program Manager

There is considerable data to indicate that cyclic exposure to immersion electrolyte followed by a period of drying, then re-immersion in electrolyte, drying, re-immersion, etc., is a better test protocol for ranking and lifetime prediction than continuous immersion. This seems to be true if electrochemical measurements (ENM or EIS) are the mode of observation, or if subjective rankings for failure are used (ProHesionTM test protocol). The Dutch group headed by DeWit at Delft/TNO using EIS + a CPE element in modeling of behavior, and the considerable amount of work by Skerry^{i,ii,iii,iv} & automotive test workers on the use of Cyclic testing to replace ASTM B117 Continuous Salt Fog Testing^v. We need to do the following in addition to our standard test protocols for EIS and ENM based on continuous immersion:

1. Prepare panels as normal using the PVC pipe set-up. Then immerse the exposed part of the panels by adding dilute Harrison's solution or by using the electrolyte composition of rainwater typical of an exposure at a high corrosion rate Air Force Base - probably the east or west coasts or Warner-Robbins.
2. As the immersion fluid is added, begin ENM measurements for the first 24 hours at the highest data acquisition rate practical, then reduce the sampling frequency to the regular 0.5 Hz as the data comes to a steady state.
3. Measure the time for each cycle to reach steady state.
4. When the R_n data indicates a relative steady state, then perform EIS measurements.
5. Perform measurements ENM & EIS for a week following the regular protocol.
6. Remove most of the electrolyte and then let dry for one week.
7. Again add the same amount of the original immersion electrolyte and repeat steps 2-6.
8. Continue the immersion/drying cycles until "failure" as defined in some context - visible failure, drastic restriction in R_n or $|Z|$ occurs
9. Compare to the continuous immersion data for the same solution.

We can couple this type of testing to thermal cycling if we run the tests in a CorroCell. What we will need to do is to do thermal analysis by DSC on the coatings to determine the wet and dry T_g of the film in the manner used with the pipeline coatings, and then try stressing the coating on exposure or re-exposure by heating it during the time of immersion. We will have to try heating at temperatures below the T_g and also above the T_g and also examine the effects of length of time a sample is held at the individual temperatures will do to the system. We can also take the samples out and monitor the changes in the coating thermal properties due to the cycling, i.e. is the T_g changed in the cycling, do we have water pick-up as

Further work will be cyclic testing in the Prohesion Cabinet, and then take out samples for

measurement using our standard immersion protocol. In this case, we may wish to consider using O-rings and clamps for sample configuration, which can then be removed to put the sample back in the exposure chamber.

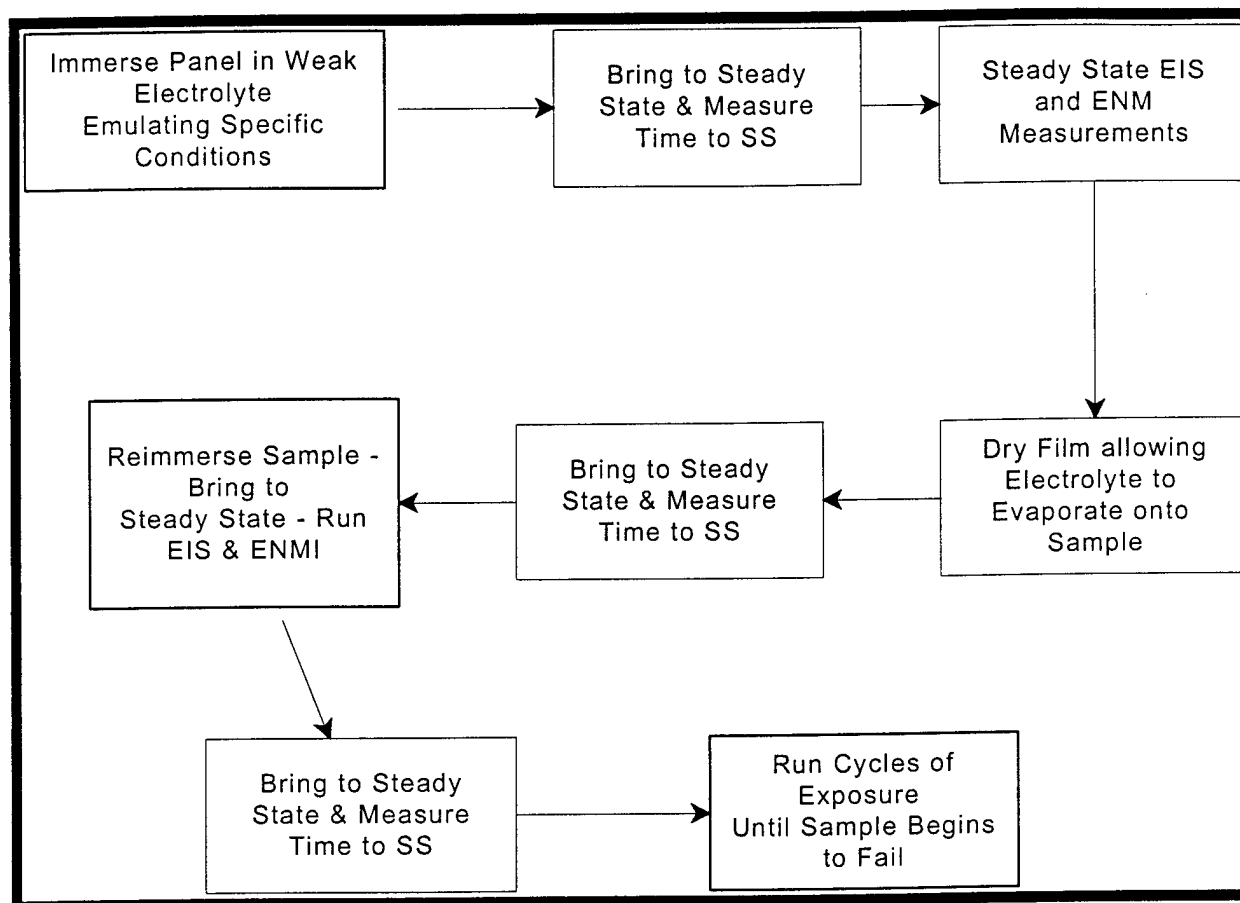


Figure (1) Future Test Protocol

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Electrochemical, Appearance, and Contact Angle Measurements on Coated Aluminum Alloy Panels under QUV/Prohesion Exposure

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Major Paul Trulove, Program Manager

This part of the annual report will cover tested panel preparation/handling, QUV/Prohesion accelerated weathering and corrosion testing protocol, electrochemical characterization, as well as gloss, color, and contact angle measurements.

So far, Batch 2 of the tested panels coated with DEFT aircraft coatings has been exposed to the QUV/Prohesion environment for 40 weeks, and Batch 3 for 15 weeks. Electrochemical Noise Method (ENM), Electrochemical Impedance Spectroscopy (EIS), gloss, color, and contact angle/surface energy measurements have been performed on these panels every week.

By the electrochemical data and visual assessments, we can see that, after 40 weeks of exposure, the systems [Batch 1](Self-Priming Topcoat) and (Primer + Glossy Topcoat) still remain at relative high level of corrosion protection, and no significant coating failures have been visually observed. However, the system (Primer + Flat Topcoat) degraded fast and essentially lost its corrosion protective ability after 12 weeks of exposure. To date, [Batch 3](Primer + Extended Life Topcoat) system has been tested for 15 weeks and showed good corrosion protection performance with little changes in its resistance values. From gloss and color data, we can see that the system (Primer + Glossy Topcoat) has excellent gloss retention while the system (Self-Priming Topcoat) lost its gloss quickly. Both of these two systems have good color maintenance. The system (Primer + Flat Topcoat) changed its color rapidly to a large degree. Due to roughness development and possible oxidation on the coated panel surface with the QUV + Prohesion exposure, the measured contact angles for all the systems decreased.

Conclusions

QUV/Prohesion accelerated weathering and corrosion testing protocol is one of the best commercially available standardized methods to accelerate corrosion process. By including the effects of electrolyte wet/dry cycling and UV together, this testing protocol may be used to facilitate the corrosion protection evaluation and ranking, especially for those systems with fair quality coatings. ENM and EIS were effective to evaluate and rank corrosion protection of the aircraft coatings and, in long term, gave us similar corrosion rating for the tested systems. The changes in coating surface appearance, such as gloss and color gave us initial sign of coating failure. Contact angle measurement revealed that adsorption of corrosive species to coated panel surface became easier with longer exposure time due to the increase in surface energy on the

coated panel surface. For the tested systems, (yellow primer) system has rapidly lost its corrosion protective ability, and (primer + flat topcoat) system has shown poor corrosion resistance. After 15 weeks of exposure, (Primer + Extended Life Topcoat) systems still showed good corrosion resistance. So far, after 40 week exposure time, both the systems (Self-Priming Topcoat) and (Primer + Glossy Topcoat) stay at very high level of corrosion resistance and only slight difference has shown in their resistance values, which implied a longer exposure or a more aggressive weathering and corrosion environment is needed to distinctly differentiate their corrosion resistance

Continuous Electrochemical, Appearance, and Contact Angle Measurements on Coated Aluminum Alloy Panels under QUV/Prohesion Exposure

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Program Manager: Lt. Colonel Paul Trulove

Summary

As part of our research efforts to develop a reliable, fast, and compressive protocol for characterizing corrosion protection of coated metal systems, experiments on coated aluminum alloy panels under extended QUV/Prohesion exposure are continuously conducted. Electrochemical Noise Method (ENM), Electrochemical Impedance Spectroscopy (EIS), gloss, color, and contact angle/surface energy measurements, as well as visual assessments have been performed on these panels every week to investigate corrosion protection of aircraft coatings.

By the electrochemical data and visual assessments, we can see that, after 86 weeks of exposure, the systems (Self-Priming Topcoat: SPT) and (Primer + Glossy Topcoat: GT) still remain at very high level of corrosion protection, and no significant coating failures have been visually observed. To date, (Primer + Extended Life Topcoat: ELT) system has been exposed for 66 weeks and has shown very good corrosion protection with little changes in its color. From gloss and color data, we can see that the system GT has excellent gloss retention while the system SPT has lost its gloss quickly. Both of these two systems have good color retention after 37 weeks of exposure, and, after that exposure time, the system GT still exhibits excellent color retention but the system SPT has changed its color rapidly. Due to roughness and possible oxidation on the coated panel surface, the measured contact angles for all the systems decreased with exposure time.

Conclusions

Corrosion characterization and lifetime prediction of the aircraft coatings on aluminum alloy were performed. For the tested systems, (yellow primer) system has rapidly lost its corrosion protective ability, and FT system has shown poor corrosion resistance. After 66 weeks of exposure, ELT system still showed very good corrosion resistance and color retention, which were similar to GT. So far, after 86 week exposure time, both the systems SPT and GT stayed at very high level of corrosion resistance, and only slight difference has shown in their resistance values. However, SPT system has exhibited much poorer appearance preservation than GT.

Corrosion Sensor Development

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Summary

We continued our studies on novel electrode configurations that are compatible with corrosion sensor use, and compared them to our normal Electrochemical Impedance Spectroscopy (EIS) and Electrochemical Noise Method (ENM) configurations under immersion conditions. Besides the 2-electrode EIS configuration that was described in our last year's report, a new 3-electrode EIS configuration also shows promise for field usage. In an effort to alleviate the polarization side effect that often occurs when no secondary reference electrode is implanted in the cell system, a new EIS testing technique called hybrid EIS has been tried. In our ENM configuration studies, Fast Fourier Transform (FFT) and Maximum Entropy Method (MEM) has been used to calculate and compare the spectra noise resistance (R_{sn}) obtained from different setups. Work has also been started on the investigation of the feasibility of corrosion sensors and the new electrode configurations for atmospheric corrosion monitoring. EIS and ENM tests were performed directly inside Prohesion chamber on coated samples with surface-attached corrosion sensors (made by DACCO Inc.). To alleviate the problems associated with surface-attached sensors, we have designed and investigated an embedded corrosion sensor technique, which has several advantages over the surface-attached sensor technique: protecting sensors surface from environment attack; improved isolation between sensors, improved measurement by ENM on small samples; better adhesion to underlying film; and higher sensitivity to small changes in coating impedance. The method shows potential for monitoring the impedance change of each coating layer during different exposure conditions, and may be useful for studying the corrosion/degradation mechanism as well as designing new accelerated testing protocols for faster ranking and better simulation of outdoor exposure. The applicability of this embedded sensor technique was studied with EIS and ENM using an embedded Pt wire sensor both in Prohesion cycling and humidity chamber.

Conclusions

Our results from immersion studies indicated that HEIS and PEIS techniques yielded identical results, and the new 3-electrode EIS setup also gave results identical to those from the conventional setup.

The variation in OCP during EIS measurement might distort the EIS spectra, especially in low

frequency range. If the OCP change is relatively large, PEIS technique may cause damage to the sample, hence is no longer feasible. In this case, HEIS may be used as an alternative technique. However, if the variation in OCP is relatively small, PEIS may give smoother spectra than HEIS does.

Good agreement was found between the new ENM configuration (Figure 12) and the conventional ENM setup during immersion test. In an well controlled non-immersion condition, (constant humidity and temperature during measurement, system is in steady state), this setup gave very good noise data. Even in the extremely unfriendly testing condition, (as in Prohesion cycling) where EIS could not give smooth spectra, and PEIS might even cause damage to the sample, this ENM setup might still be able to give R_n that reflected at least in some degree how the polarization resistance changed along time. As far as we can tell, this is the first time such *in situ* electrochemical measurements have been made in a corrosion test chamber. The simple (embedded wire electrode + ENM measurement) is definitely a sensor system that could be utilized on an aircraft for a possible need-based maintenance system.

The embedded corrosion sensor has certain advantages over surface attached sensors: improved sensor reliability by protecting sensor from environment attack; improved isolation between sensors, applicability for ENM measurements on small samples; better adhesion to underlying film; higher sensitivity to small change in coating impedance; capability for monitoring the impedance variation of each coating layer during different exposure conditions; potential utility for studying the corrosion/degradation mechanisms as well as designing new accelerated testing protocols for faster ranking and better simulation of outdoor exposure.

Use of Electrochemical Testing Methods for in situ Corrosion Monitoring

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Program Manager: Lt. Colonel Paul Trulove

Abstract

Continued efforts were made to develop a practical corrosion sensor that could be used for in situ monitoring of corrosion. A short review is given in this report describing how this project is proceeding at NDSU. Our studies indicated that electrochemical Noise Method (ENM) is somehow the best way to monitor corrosion on field over long time period without bringing any artificial damage or even perturbation to the system. The results obtained through our in situ ENM measurement showed a clear decreasing trend as the environmental humidity increased or as the aging time increased, implying possible film degradation and onset of corrosion. Potentiostatic Electrochemical Spectroscopy (PEIS) may be applied to monitor corrosion in "ideal" exposure condition in which the system is in steady state during the entire measurement. However, it cannot be applied when the system is in a fast changing environment. Hybrid EIS (HEIS) is somehow "safer" than PEIS since it brings less artificial damage to the sample being tested, but it has a narrower measurable impedance range than PEIS, and when the impedance becomes higher as a result of decreasing humidity, HEIS may no longer give valid result. Galvanostatic EIS is not applicable for measuring coating /metal system over broad frequency range due to its inherent limitations.

Conclusions

The non-immersion exposure studies indicated that EIS may be applicable to monitor corrosion in "ideal" exposure condition in which the system is at steady state during the measurement. PEIS is capable of measuring higher impedance (has a broader measurable impedance range) than HEIS, therefore, PEIS is more appropriate for measuring impedance at low humidity level. However, PEIS may cause artificial damage to the sample and may not be used when the system is in non-steady state or in a fast changing environment. GEIS is not applicable for measuring impedance over a broad frequency range due to its inherent limitations. HEIS is somehow "safer" than PEIS since it may bring less artificial damages to the sample, and it can be applied to measure impedance at high frequency range during the Prohesion cycling test. However, HEIS has a narrower measurable impedance range than PEIS.

Similar testing based on ENM indicated that ENM has the capability of recording data without leaving any negative effect to the sample in any kind of exposure conditions. The calculated R_n and R_{sn} showed clear decreasing trend as the environmental humidity increases or as the aging time increases, implying possible film degradation and onset of corrosion. Therefore, ENM may be used to monitor the degradation of coating film and give early warning of the onset of corrosion.

**Magnesium Powder Filled Primer and Extended Lifetime™ Topcoat for Cathodic
Protection of 2024 T-3 Aluminum Alloy**

Presented in

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Program Manager: Lt. Colonel Paul Trulove

Abstract

500 hours direct exposure of 2024 T-3 aluminum panels to Prohesion™ cycling in Harrison's solution causes rapid corrosion of the alloy to occur. Coating the alloy with an epoxy primer filled with 20 to 200 micron sized magnesium powder, at or above CPVC (critical pigment volume concentration) cathodically protects the alloy for up to 2,000 hours. Cathodic protection of a primed panel appears to occur in two distinct stages, initially, closely packed metal particles connect in the primer to form a conductive and sacrificial path thus circulating charge. Gradually, as the surface of the metal is oxidized porous hydroxides, $[MgO, Mg(OH)_2]$ [brucite] domains grow and interconnect providing a conductive path for charge to flow, thus extending the period of protection of that alloy's surface. It is not the surface of the coating that is important but the bulk of the primer. Putting on the topcoat slows down the direct acid solution contact with the Mg particles as well as filling the pores in the primer. The cathodic protection still takes place, but the reactive consumption of the Mg slows considerably. Anode particle-particle contact extending away from the scribe and throughout the body of the primer is believed to contribute to the cathodic protection of the alloy. It is thought that "how fast" the exposed anode in the scribe is consumed is a kinetic parameter that influences the dissolution of magnesium and its hydroxides along the scribes over the panel and is related to topcoat PVC, magnesium particle size, and packing. Overall our data indicates that using a topcoat over a Mg-rich primer at its CPVC, the coating systems protection to the 2024 T-3 aluminum both cathodically and passively for up to 3000 hours Prohesion™ exposure before damage to system begins to spread from the scribe.

Summary

The complete coating system for cathodic protection of 2024 T-3 aluminum with a magnesium powder primer begins at the alloy interface with an organo-silane adhesion promoter that is integral to the binder itself. A moisture cure aromatic isocyanate binder comprises the backbone of the primer polymer adding high chemical and alkaline resistance improved adhesion, flexibility, and wetting of both pigment and alloy surface. Ideal magnesium particle size distribution should range from 10 to 200 microns. As submicron sized magnesium is rapidly consumed and acts to over accelerate cure of primer binder.

Overall, it is believed that with the correct pigment volume relationships, particle size, and polymeric binder, and formulation procedures top-coated magnesium powder primer coating systems are capable of protecting the 2024 T-3 aluminum both cathodically and passively for over 3000 hours Prohesion™ exposure before the onset of damage to the polymer occurs at the scribe.

Continuous Electrochemical, Appearance and Contact Angle Measurements on Coated Aluminum Alloy Panels under QUV/Prohesion Exposure

Presented in

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Annual Project Report

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To: U.S. Air Force Office of Scientific Research

Program Manager: Lt. Colonel Paul Trulove

Summary

The research effort to develop a fast, reliable and comprehensive protocol to characterize corrosion protection of coated 2024 aluminum has been investigated under extended QUV/Prohesion exposure. Details of these techniques are given in pre 2000 annual reports. Electrochemical Noise Method (ENM), Electrochemical Impedance Spectroscopy (EIS), gloss, colour and contact angle/surface energy measurements, in addition to visual assessment have been made on the panels at weekly intervals to investigate corrosion protection of aircraft coatings. By a combination of the measurement techniques a protocol has been established for characterization of coating systems. A mathematical life-time prediction model for coatings has been developed using data from electrochemical techniques; results have correlated with visual observations of coated panels.

The findings from the research have been compiled as Chapter 5 of the PhD thesis submitted by Junping Li. Chapter 5 was attached as reference for Section 2 (Major Accomplishments) of the 2001 annual report.

Conclusions

A comprehensive characterization protocol has been developed and implemented for testing aircraft coatings.

Using a combination of electrochemical techniques, appearance assessments, surface characterization and visual inspection, a series of aircraft coating systems have been ranked successfully across a range of poor to excellent performance.

Electrochemical data from this work has been analyzed and found to fit an exponential decay model. This model has given reasonable lifetime predictions on coated aluminum alloy systems.

UV/Prohesion accelerated weathering were found to be among the best commercially available methods for testing protective coating systems on 2024 series aluminum alloy.

Electrochemical Noise Method and Electrochemical Impedance Spectroscopy both gave consistent ratings of the coating systems under test. Electrochemical techniques were a useful tool in the study of mechanistic processes and protective mechanisms of organic barrier coatings with and without chromate.

Gloss and color measurement complimented the data obtained by electrochemical techniques.

Full conclusions of Chapter 5 can be found section 5.5, page 219 and a reference list for this chapter can be found 5.6, page 222.

Chapter III

**Contribution of
Prof. Dennis Tallman
Department of Chemistry**

Summary of Research Activities and Results FY 1997 through FY 2000

Major Accomplishments:

Detailed in section below.

Equipment Additions:

Scanning Probe Microscope Upgrade. The Nanoscope E (Digital Instruments) Scanning Probe Microscope (SPM), previously purchased on a Department of Defense EPSCoR instrumentation grant, has now been upgraded to a Nanoscope IIIA. This upgrade extends the imaging capability of the SPM to include (in addition to the contact mode capability of the earlier instrument) non-contact, lateral force, magnetic force, electrical force and tapping mode modes. Additionally, the Extender Electronics Module was added to provide phase imaging capability, permitting detection of variations in composition, friction, adhesion, stiffness, viscoelasticity and surface properties. The tapping mode imaging and the phase imaging capabilities are anticipated to be particularly useful for the study and characterization of polymer surfaces.

AFM Scanner Addition. To complement the AS-130 AFM scanner (125 μ m x 125 μ m range) of the above instrument, a new AS-12 scanner (10 μ m x 10 μ m) has been added. This scanner has higher resolution capability and should permit us to observe individual polymer molecules on metal surfaces. This scanner has been installed and calibrated and we are now beginning to use it in our imaging studies. We have some residual vibration problems to correct, but we are close to achieving atomic resolution on mica with this scanner (a test of performance). All work described below was performed on the AS-130 scanner.

Scanning Vibrating Electrode Technique. The scanning vibrating electrode technique permits the mapping of current density in an electrolyte immediately above a substrate surface. The instrument used in this study was from Applicable Electronics (Forestdale, MA). A microelectrode, an electrochemically etched Pt/Ir (80%/20%) wire coated with parylene and arced at the tip to expose the metal, is platinized to form a small ball of platinum black at the tip, approximately 20 microns in diameter in this study. This electrode or probe is vibrated in two dimensions (parallel and perpendicular to the surface, approximately one tip diameter in each dimension) as the tip is rastered above the surface of the substrate at a height of ca. 100 microns. Current flow in the electrolyte due (for example) to corrosion processes occurring on the substrate surface results in a voltage (IR) drop within the electrolyte. This voltage drop is sensed by the vibrating probe and resolved by two phase-sensitive detectors into a voltage vector having

magnitude and direction. The voltage vector is converted into a current density vector using calibration data generated in a separate experiment (calibration involves generation of a known current density from a point source calibration electrode). The measured current density vectors permit a mapping of both the magnitude and direction of current flow immediately above the substrate surface. This current density map can be overlaid onto an optical micrograph of the substrate captured by a video microscope. This capability permits correlation of anodic and cathodic current processes with visual features on the substrate surface. The SVET is capable of providing detailed spatially resolved information not readily obtainable by other techniques.

Computers/Electronics. Multiple computers and small electronics have also been added.

Personnel Contributing to this Study:

D.E. Tallman, G. Chen, C.S. Jeffcoate, Y. Pae, B. Reems, V.J. Gelling, J. He, and X. Yang.

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Presentations at Technical Meetings:

"Electronically Conducting Polymers and Corrosion," 6th International Symposium on Electrochemical Methods in Corrosion Research, August 25-29, 1997, Trento, Italy.

"Studies of Electronically Conducting Polymers for Corrosion Inhibition of Aluminum and Steel," with Y. Pae, G. Chen, G. P. Bierwagen, B. Reems and V. Gelling, ANTEC 98, Society of Plastics Engineers, April 27-30, 1998, Atlanta, GA, **Invited Speaker.**

"Studies of Electronically Conducting Polymers for Corrosion Inhibition of Steel and Aluminum," with Y. Pae, G. P. Bierwagen, V. Johnston-Gelling, B. Reems and J. He, Electroactive Polymers for Corrosion Protection Workshop, Sponsored by the Office of Naval Research, January 5-6, 1999, Washington, DC, **Invited Speaker.**

"Scanning Vibrating Electrode Studies of Electronically Conducting Polymers for Corrosion Control of Steel and Aluminum," with J. He, V. Johnston-Gelling and G. P. Bierwagen, Gordon Research Conference on Electrochemistry, January 17-21, 1999, Ventura, CA, poster presentation.

"DSP-Based Instrumentation for Electrochemical Impedance Spectroscopy," with D. Farden and G. Miramontes de León, Electrochemical Society Meeting, May 2-7, 1999, Seattle, WA, **Invited Presentation.**

"AFM and SEM Studies of Aircraft Coatings under Accelerated Weathering Tests," with X. F. Yang and G. P. Bierwagen, The 1st International Conference on Scanning Probe Microscopy of Polymers, August 27-29, 1999, Santa Barbara, CA, poster presentation.

"Studies of Inherently Conducting Polymers for Corrosion Inhibition of Aluminum and Steel," with V. Johnston-Gelling, J. He and G. P. Bierwagen, 14th International Corrosion Congress, September 26-October 1, 1999, Cape Town, South Africa.

"Application of the Scanning Vibrating Electrode Technique for Probing Interactions between Conductive Electroactive Polymers and Active Metals," with Victoria Johnston Gelling, Jie He, Gordon P. Bierwagen, and Gordon G. Wallace, 11th Royal Australian Chemistry Institute

Conference (RACIC), February 6-11, 2000, Canberra, ACT, Australia, **Invited Presentation**.

"The Scanning Vibrating Electrode Technique and its Application to the Study of Corrosion Processes," Joint North Dakota, South Dakota and Minnesota Academy of Sciences Meeting, Symposium on "Electrochemistry and Characterization of Complex Surfaces," April 28, 2000, Moorhead, Mn, **Invited Presentation**.

"A Rapid Corrosion Resistance Test Protocol for Organic Coatings Systems: Thermal Cycling + Impedance Measurements," with Lingyun He and Gordon Bierwagen, 197th Meeting of the Electrochemical Society, May 14-18, 2000, Toronto, Canada, **Invited Presentation**.

"Electrode Configurations for *In Situ* Electrochemical Impedance Measurements On Coated Metal Systems," with Xianping Wang and Gordon Bierwagen, 197th Meeting of the Electrochemical Society, May 14-18, 2000, Toronto, Canada, poster presentation.

"Characterization of Aircraft Coatings by Electrochemical Impedance Spectroscopy," with Moussa Zidoune, Junping Li and Gordon Bierwagen, 197th Meeting of the Electrochemical Society, May 14-18, 2000, Toronto, Canada, poster presentation.

"Electroactive Conducting Polymer Coatings for Corrosion Protection," 32nd American Chemical Society Great Lakes Regional Meeting, Symposium on "Coatings Materials for the 21st Century," June 4-7, 2000, Fargo, ND, **Invited Presentation** (symposium co-organizer).

"Electroactive Conducting Polymers for Corrosion Control: Studies of Poly(3-Octyl Pyrrole) and Poly(3-octadecyl pyrrole) on Aluminum 2024-T3 Alloy," with Victoria Johnston Gelling, Michelle Wiest, Gordon P. Bierwagen and Gordon G. Wallace, 26th Annual Conference on Organic Coatings, July 3-7, 2000, Athens, Greece, **Invited Presentation**.

"Scanning Vibrating Electrode Studies of Electronically Conducting Polymers on Aluminum Alloy," with Jie He, Victoria Johnston Gelling and Gordon P. Bierwagen, 220th National American Chemical Society Meeting, Symposium on "Electroactive Polymers for Corrosion Control/Prevention," August 20-24, 2000, Washington, DC, **Invited Presentation**.

"Study of Poly(3-Octyl Pyrrole) for Corrosion Control of Aluminum 2024-T3," with Victoria Johnston Gelling, Gordon P. Bierwagen and Gordon G. Wallace, 220th National American Chemical Society Meeting, Symposium on "Electroactive Polymers for Corrosion Control/Prevention," August 20-24, 2000, Washington, DC, poster presentation.

"A Scanning Vibrating Electrode Study of Chromated-Epoxy Coatings on Steel and Aluminum," with Jie He, Victoria Johnston Gelling and Gordon P. Bierwagen, 220th National American Chemical Society Meeting, Symposium on "Electroactive Polymers for Corrosion Control/Prevention," August 20-24, 2000, Washington, DC, poster presentation.

"Electrochemical Methods for Corrosion Research" and "Electroactive Conducting Polymers for Corrosion Control," Nankai University, October 9, 2000, Tianjin, China, **Two Invited Lectures**.

"Electrochemical Methods for Corrosion Research" and "Electroactive Conducting Polymers for Corrosion Control," Shandong Normal University, October 13, 2000, Jinan, China, **Two Invited Lectures.**

"Electrochemical Methods for Corrosion Research" and "Electroactive Conducting Polymers for Corrosion Control," North China Institute of Technology, October 16, 2000, Taiyuan, China, **Two Invited Lectures.**

"Electrochemical Methods for Corrosion Research" and "Electroactive Conducting Polymers for Corrosion Control," Central Iron and Steel Research Institute, October 19, 2000, Beijing, China, **Two Invited Lectures.**

International Seminars Presented:

"Corrosion, Coatings, Conductive Polymers and Electrochemical Methods for their Study," Workshop on Corrosion Protection using Conducting Polymers, September 14-16, 1997, University of Wollongong, Wollongong, Australia, **Invited Speaker.**

"Electronically Conducting Polymers and Corrosion," Workshop on Corrosion Protection using Conducting Polymers, September 14-16, 1997, University of Wollongong, Wollongong, Australia, **Invited Speaker.**

"The Scanning Vibrating Electrode Technique and its Application to the Study of Corrosion Processes," The University of Wollongong, November 23, 1999, Wollongong, NSW, Australia, **Invited Lecture.**

"The Scanning Vibrating Electrode Technique and its Application to the Study of Corrosion Processes," Commonwealth Scientific and Industrial Research Organization (CSIRO), March 30, 2000, Melbourne, Australia, **Invited Lecture.**

"Electrochemical Methods for Corrosion Research" and "Electroactive Conducting Polymers for Corrosion Control," Nankai University, October 9, 2000, Tianjin, China, **Two Invited Lectures.**

"Electrochemical Methods for Corrosion Research" and "Electroactive Conducting Polymers for Corrosion Control," Shandong Normal University, October 13, 2000, Jinan, China, **Two Invited Lectures.**

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"Electrochemical Methods for Corrosion Research" and "Electroactive Conducting Polymers for Corrosion Control," Central Iron and Steel Research Institute, October 19, 2000, Beijing, China, **Two Invited Lectures.**

Graduate Theses:

Brent Reems, "Evaluation of Corrosion Protective Properties of the Electroactive Conducting Polymers Polyaniline and Polypyrrole using Electrochemical Techniques", Master Degree, January 2000.

Victoria Johnston Gelling, "The Study of Polypyrrole as a Corrosion Inhibitor of Aluminum Alloy 2024-T3", PhD Dissertation, September 2001.

Use of a sol-gel conversion coating for aluminum corrosion protection

D. E. Tallman and G. P. Bierwagen, co-PIs

Abstract. In this study, the behavior of a sol-gel conversion coating alone and in combination with a polyurethane uncoat (TT-P-2756 self-priming topcoat) on Al 2024-T3 alloy was investigated under immersion in dilute Harrison's solution {3.5g/l $(\text{NH}_4)_2\text{SO}_4$, 0.5g/l NaCl}. The sol-gel coating consisted of SiO_2 and ZrO_2 with a ratio of 3.4:1. The evolution of the coating system under immersion was followed by atomic force microscopy (AFM), scanning electronic microscopy (SEM), electrochemical impedance spectroscopy (EIS), and X-ray photoelectron spectroscopy (XPS). It was found that though pitting corrosion and degradation products on the sol-gel single coating surface were observed after 2 days of immersion, further pitting corrosion ceased after a few days of immersion. Under-coating blisters in the sol-gel plus polyurethane topcoat system were found at 4 weeks of immersion, after which no further increase in size of the blisters was observed. It is conjectured that aluminum oxide and silicon oxide may form a stable mixed oxide barrier layer at the interface after initial corrosion, which prohibits further pitting corrosion development.

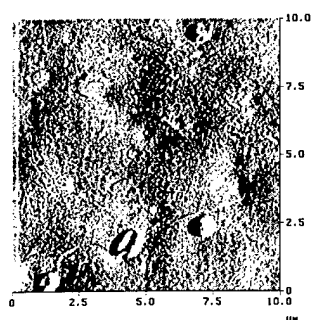
Conclusions. The sol-gel coating inhibits the local dissolution on the aluminum surface. The EIS measurement shows that when Al bare alloy was immersed in dilute Harrison's solution, the impedance modulus increased initially and then decreased over the next 4 weeks. In contrast, the impedance modulus of the sol-gel coated Al alloy increased steadily during the first 4 weeks of immersion. Therefore, sol-gel coating stabilized the protecting layer on the aluminum surface.

Publication. X.F. Yang, D.E. Tallman, V.J. Gelling, G.P. Bierwagen, L.S. Kasten, J. Berg "Use of a Sol-Gel Conversion Coating for Aluminum Corrosion Protection", *Surface and Coatings Technology*, 140 (2001) 44-50.

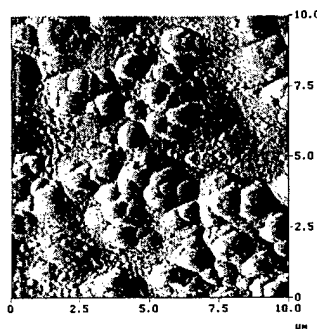
WEATHERING DEGRADATION OF A POLYURETHANE COATING

D. E. Tallman, G. P. Bierwagen and S. G. Croll, co-PIs

Abstract. The degradation of polyurethane topcoat over a chromate pigmented epoxy primer was examined by Atomic Force Microscopy (AFM), Scanning Electronic Microscopy (SEM), X-ray Photo-electron Spectroscopy (XPS) and Fourier Transform Infrared Spectroscopy (FTIR) after the coated panels were exposed in a QUV chamber. It was found that upon QUV exposure, blisters formed on the topcoat surfaces during the initial phase of coating degradation. As a result of blister formation and subsequent breakage, coating gloss was lost before any pigments were exposed in the coating. XPS and FTIR analysis indicated that urea and urethane group concentrations increased in the coating upon exposure. It is suggested that the build-up of hydrophilic groups in the coating during coating degradation promoted water absorption into the coating system, then the alternating dry and wet environment caused the formation of osmotic cells and thus blisters on the coating surfaces.



Before exposure



9 weeks Exposure

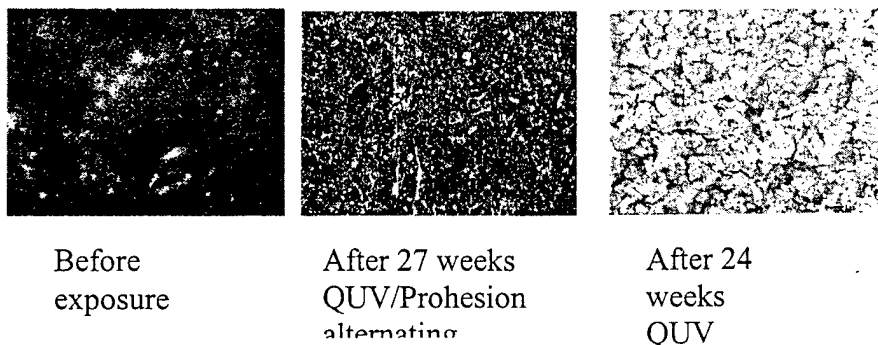
Conclusions. 1). At an early coating degradation stage, blister formation was observed on the glossy polyurethane coating surface. Their development and breakage was part of the coating surface damage, which resulted in the initial loss of the coating gloss. Pigments were exposed subsequent to this initial loss of gloss. 2) A proposed mechanism of blister formation is as follows: When the coating was degraded under the combined function of UV, water and oxygen, soluble degradation products concentrated in the coating. As a result, additional water was adsorbed into the coating, which in turn formed osmotic cells under the coating surface layer. With the cycling of water adsorption and desorption, the osmotic cells continue to develop and the coating surface became blistered. 3) Both hard and soft chain segment scissions at the film-air interface were found to be dependent on exposure cycling of UV/H₂O radiation. Therefore, after exposure, the formation of urea groups was more noticeable at the coating film-air surface than within the bulk of the coating. 4) Results obtained from AFM and particularly FTIR indicate strong evidence for the formation of hydrophilic degradation products such as polyurea. These products may provide some of the materials that promote osmotic forces within the top layer of the coating and thereby blistering. Other decomposition and oxidation products may form in the coating and thus provide additional contributions to the osmotic pressure.

Publication. X. F. Yang, C. Vang, D. E. Tallman, G. P. Bierwagen, S. G. Croll, S. Rohlik, "Weathering Degradation of the Polyurethane Coating," *Polymer Degradation and Stability* (2001) in press.

BLISTERING AND DEGRADATION OF POLYURETHANE COATINGS UNDER DIFFERENT ACCELERATED WEATHERING TESTS

D. E. Tallman, G. P. Bierwagen and S. G. Croll, co-PIs

Abstract. In this study, two groups of accelerated weathering tests were conducted on a glossy polyurethane aircraft coating. One was exposing the coated panel in a QUV chamber only and the other was exposing the coated panel in the QUV chamber and a Prohesion chamber alternatively. AFM imaging found that micro blisters formed on the coating surface under both exposure conditions, but they developed in different ways. SEM showed that the coating was damaged more under QUV exposure than under QUV/Prohesion alternate exposure. By examining the coating after 9 weeks of QUV exposure and after 25 weeks of QUV/Prohesion exposure with XPS and SEM, we concluded that the coating oxidation that occurred under QUV exposure resulted in the formation of carboxyl group products and volatile products, while the coating oxidation that occurred under QUV/Prohesion alternate exposure caused the formation of C-O bonds in the coating during the exposure period.



Conclusions.

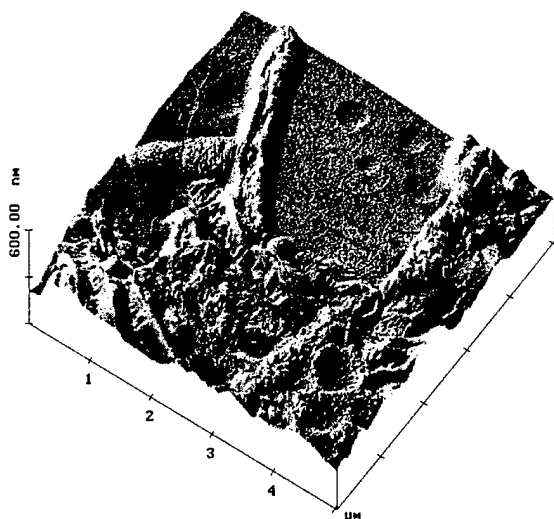
1. When a polymer coating is placed in a wet/dry alternating environment, blisters of sub-micrometer to micrometer dimension form on the coating surface. A high temperature and long wet period promote development of larger blisters.
2. Before pigment exposure, this blister development causes the initial loss in coating gloss that is observed.
3. UV radiation and high temperature play the main role in weathering coating degradation. QUV exposure appears to be a more destructive exposure condition than QUV/Prohesion alternating exposure.
4. The main oxidation products under QUV exposure are carboxyl group products and volatile and/or soluble products, while C-O formation is the main result of oxidation during 25 weeks of QUV/Prohesion exposure (perhaps from formation of hydroperoxides).

Publication. X. F. Yang, D. E. Tallman, G. P. Bierwagen, S. G. Croll, S. Rohlik, "Blistering and Degradation of Polyurethane Coatings under Different Accelerated Weathering Tests," *Polymer Degradation and Stability* (2001) submitted.

Hydrolytic Degradation of Polyurethane Coatings

D. E. Tallman, G. P. Bierwagen and S. G. Croll, co-PIs

Abstract. When a polyurethane self-priming coating on a sol-gel treated aluminum panel was immersed in dilute Harrison's solution, subsequent coating degradation was inspected with Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), X-ray Photoelectron Spectroscopy (XPS) and Chemical Force Microscopy (CFM). After immersion, filiform threads formed in the coating surface. XPS results showed that the coating surface was undergoing oxidation in the solution. The mechanism suggested for the formation of filiform structures is when the coating is immersed in the solution, it penetrates into the coating and causes hydrolytic degradation of the coating. The soluble degradation products promote water adsorption into the coating that results in the formation of blisters on the surface, especially at low cross-linked locations. The combination of blisters appears as filiform structures on the coating surface.



Conclusions. When a polyurethane coating was immersed in dilute Harrison's solution, micro-scale filiform threads developed in the coating surface. The filaments appear to be caused by hydrolytic degradation of the coating that is suggested to occur initially in regions of low cross-link density. It is proposed that during coating degradation, soluble degradation products are formed that concentrate in the coating near the surface, leading to the uptake of additional water. This process results in the formation of very small blisters, and it is the coalescence of these fine blisters that initiates filiform structures. The size of these filiform structures varied over a wide range, probably the result of variations in the local coating environment.

Publication. X. F. Yang, D. E. Tallman, G. P. Bierwagen, S. G. Croll, L. S. Kasten, S. Rohlik "Hydrolytic Degradation of Polyurethane Coatings", *Polymer Degradation and Stability* (2001) accepted for publication.

Degradation of Low Gloss Polyurethane Aircraft Coatings under UV and Prohesion Alternating Exposures

D. E. Tallman, G. P. Bierwagen and S. G. Croll, co-PIs

Abstract. In this work, by using AFM, SEM/EDX, XPS and EIS, we studied weathering degradation occurred on two types of low gloss polyurethane aircraft coatings: one was a traditional matte polyurethane coating and the other was a fluorinated polyurethane coating, also called the Extended Life Topcoat (ELT). The accelerated weathering tests were carried out in a QUV chamber and a Prohesion chamber alternately. It was found that coating oxidation was the main coating degradation mode in both coatings. The matte coating cannot stop water penetration effectively, so the coating was destroyed after 25 weeks. The ELT coating was still functional after 83 weeks exposure. EDX analysis also showed the different behaviors of Al, Ti and Si containing pigments under the exposure.

Conclusions.

1. Compared with the matte coatings, the ELT shows superior weathering durability in accelerated weathering tests. The Fluoro-urethane polymer formed voids free coating with low gloss.
2. Under QUV/Prohesion alternating exposure, the main degradation mode of the two coatings was oxidation. The oxygen in the environment reacted with coating and form compounds with C-O bond and carboxyl group products.
3. Al containing pigments were not stable in the coating. They diminished gradually during exposure. In contrast, Ti and Si containing pigments showed good durability. Therefore, Properly chosen pigments can prevent voids formation in the coating.

Publication. X. F. Yang, J. Li, D. E. Tallman, S. G. Croll and G. P. Bierwagen, "Degradation of Low Gloss Aircraft Coatings under UV and Prohesion Alternating Exposures," (2001) manuscript in preparation.

A Study of Polypyrrole as a Corrosion Inhibitor for Steel and Aluminum

Jie He,¹ Victoria Johnston Gelling,¹ Dennis E. Tallman (Co-PI),¹
Gordon P. Bierwagen (Co-PI),² and Gordon G. Wallace³

¹ Department of Chemistry and ² Department of Polymers and Coatings
North Dakota State University, Fargo, ND 58105, USA

³Intelligent Polymer Research Institute, Department of Chemistry
University of Wollongong, Wollongong NSW 2522, AUSTRALIA

INTRODUCTION

Chromated-epoxy primers are often used for corrosion control of iron and aluminum structural alloys. However, due to environmental concerns and adverse health effects surrounding such use of chromates, there is an intensive effort to find suitable replacements for chromate-based coatings. Electroactive conducting polymers (ECPs) continue to be of considerable interest as potential replacements for chromate-based coatings. ECPs, in addition to being conductive, are redox active materials, typically with potentials that are positive of iron and aluminum. Thus, as with chromate, interesting and potentially beneficial interactions of ECPs with active metal alloys such as steel and aluminum are anticipated.

In this paper, the use of electrochemical techniques for the measurement of the corrosion inhibition provided to aluminum alloy 2024-T3 (Al 2024-T3) or steel by ECP, chromated-epoxy, and plain epoxy coatings will be discussed. The ECP studied was poly(3-octyl pyrrole) doped with pTS⁻/ClO₄⁻ (POP) shown in Figure 1. The ECP was considered to be a primer coating and, thus, was occasionally studied in conjunction with a polyurethane topcoat. The use of electrochemical impedance spectroscopy (EIS) and Scanning Vibrating Electrode Technique (SVET) will be discussed with results presented.

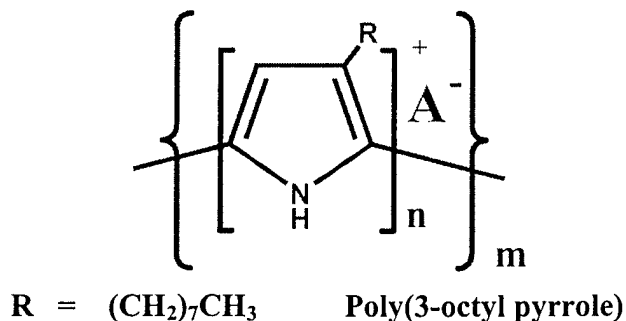


Figure 1. Structure of Poly(3-alkyl pyrrole). Where n is the number of monomer units per positive charge, usually 2 to 4, and (m x n) is the polymer size, usually ~8,000 to 10,000.

Although there were significant differences in the behavior of the POP-coated steel and POP-coated aluminum substrates as observed by SVET, both exhibited a significant delay before the onset of any observable current compared to uncoated or epoxy-coated samples. Current

density maps for the steel clearly indicate that the reduction reaction occurred on the conducting polymer surface, with oxidation confined to the defect. On the other hand, current density maps for the aluminum alloy never displayed significant oxidation at the defect. Rather, reduction (after a significant delay) occurred at the defect as well as across the polymer surface, with concomitant localized undercoating oxidation of the aluminum substrate.

Both steel and aluminum substrates coated with the chromated-epoxy exhibited a significant delay before the onset of corrosion within the scribe, compared with substrates coated with nonchromated-epoxy. Furthermore, the current density maps for steel suggest that the reduction reaction may occur at the surface of the chromated-epoxy coating. With the nonchromated-epoxy coating, the reduction reaction was always confined to the defect area.

EXPERIMENTAL

Sample Preparation and Experimental Conditions. The plain epoxy coating was a polymer of epichlorohydrin and bisphenol A (Dow Chemical D.E.R. 331) with Ancamide 2353 curing agent (Air Products). The chromated-epoxy coating was a high solids primer coating (Mil-P-23377G, DEFT, Inc.). Cold-rolled steel (Q-Panel) or aluminum alloy (Al 2024-T3, Q-Panel) samples were first polished using 600 grit silicon carbide, washed with hexane, and air-dried. After this pretreatment, the corresponding coatings were applied by bar coating and were allowed to dry overnight. The average coating thickness for the plain epoxy was $30 \pm 8.5 \mu\text{m}$, for the chromated-epoxy $21 \pm 4.5 \mu\text{m}$. The coating of each sample contained a defect that was introduced by scribing, the area of the defect ranging from 0.1 to 0.3 mm². No conversion coatings and no topcoats were utilized in this study.

The poly(3-octyl pyrrole) was synthesized electrochemically by the Intelligent Polymer Research Institute (Wollongong, Australia) and contained perchlorate and paratoluene sulfonate counterions. The synthetic details and polymer characterization have been described previously.ⁱ Briefly, the polymer was generated galvanostatically at a platinum electrode at a current density of 1 mA/cm² from a solvent mixture of CCl₄ (80%) and CH₂Cl₂ (20%) containing 0.1 M monomer (3-octyl pyrrole), 0.1 M tetrabutylammonium perchlorate and 0.025 M tetrabutylammonium *p*-toluenesulfonate. The soluble fraction of the electrosynthesized polymer was recovered from the liquor and excess electrolyte removed.ⁱ Cast films of the polymer were both electroactive (by cyclic voltammetry) and conductive (ca. 5×10^{-3} S/cm by the four-point probe technique).ⁱ

The cold-rolled steel (Q-Panel), aluminum alloy (Al 2024-T3, Q-Panel) and pure aluminum (99.998%, Alfa Aesar) substrates were first polished using 600 grit silicon carbide, washed with hexane, and air-dried. After this pretreatment, the POP coating was applied by solution casting from a 1% solution in a solvent consisting of 50% CCl₄ and 50% CH₃CN. The coatings were allowed to dry overnight. The average coating thickness was $2.3 \pm 1.6 \mu\text{m}$.

For the Al 2024-T3 samples, the immersion solution was dilute Harrison solution, containing 0.35% (NH₄)₂SO₄ and 0.05% NaCl in H₂O. For the cold-rolled steel samples, the immersion solution was 3% NaCl solution. These solutions were prepared from reagent grade salts and distilled water.

Instrumentation. The scanning vibrating electrode technique permits the mapping of current density in an electrolyte immediately above a substrate surface. The instrument used in this study was from Applicable Electronics (Forestdale, MA). A microelectrode, an electrochemically etched Pt/Ir (80%/20%) wire coated with parylene and arced at the tip to expose the metal, is platinized to form a small ball of platinum black at the tip, approximately 20

microns in diameter in this study. This electrode or probe is vibrated in two dimensions (parallel and perpendicular to the surface, approximately one tip diameter in each dimension) as the tip is rastered above the surface of the substrate at a height of ca. 100 microns. Current flow in the electrolyte due (for example) to corrosion processes occurring on the substrate surface results in a voltage (IR) drop within the electrolyte. This voltage drop is sensed by the vibrating probe and resolved by two phase-sensitive detectors into a voltage vector having magnitude and direction. The voltage vector is converted into a current density vector using calibration data generated in a separate experiment (calibration involves generation of a known current density from a point source calibration electrode). The measured current density vectors permit a mapping of both the magnitude and direction of current flow immediately above the substrate surface. This current density map can be overlaid onto an optical micrograph of the substrate captured by a video microscope. This capability permits correlation of anodic and cathodic current processes with visual features on the substrate surface. The SVET is capable of providing detailed spatially resolved information not readily obtainable by other techniques.

Samples for SVET measurement were cut into 1-cm x 1-cm squares and were masked by a Polyester 5 adhesive tape (3M Company) such that only a 2-mm x 2-mm square opening of the sample was exposed. The artificial defect was made using a scribing tool, the sample was mounted in a Teflon sample cell, and ca. 5 mL of the appropriate immersion solution was added. Scans were initiated within 5 minutes of immersion and were collected every 20 minutes for the duration of the experiment, typically 20 hours. Each scan consisted of 400 data points obtained on a 20 x 20 grid, with an integration time of 1-second per point. A complete scan required 10 minutes, followed by a 10-minute rest period prior to the next scan. The current density maps of this paper are displayed in two ways. In one method, the normal or z-component of the measured current density in the plane of the vibrating electrode is plotted in 3-dimensional format over the scan area, with positive and negative current densities representing anodic and cathodic regions, respectively. In the other method, vectors representing current density magnitude and direction are superimposed onto an optical image of the immersed sample. In all cases, the bottom edge of the optical micrograph corresponds to the x-axis of the 3-dimensional plot.

The measurements were taken at the open-circuit potential. At least six specimens of each sample type were prepared and scanned to assess reproducibility of the observed phenomena. In each case, representative scans are presented. The background noise in our SVET instrumentation was estimated to be $3 \mu\text{A}/\text{cm}^2$, determined from the standard deviation of the variations in current density at sufficiently large distance (ca. 1 mm) from the point source calibration electrode passing 60 nA of current.

Electrochemical Impedance Spectroscopy (EIS) was employed in the long-term immersion studies of the coatings on Al 2024-T3. The EIS was performed using a three-electrode configuration. The reference electrode was a saturated calomel electrode (SCE) and the counter electrode consisted of a platinum mesh electrode. A polyvinyl chloride (PVC) pipe was glued, using marine quality adhesive, onto the coated surface to serve as a reservoir for the electrolyte solution. EIS instrumentation consisted of a PC3 (or PC4) potentiostat in addition to an 8-channel multiplexer controlled by CMS100/300 software (Gamry® Instruments). Impedance measurements were carried out at the open circuit potential with a 5 mV rms amplitude perturbation over the frequency range of 5000 Hz to 0.01 Hz.

RESULTS AND DISCUSSION

Long Term Immersion Studies. EIS was used to study samples that have been under immersion for approximately 600 days. EIS data were collected at the open circuit potential for increasing times of immersion. Dilute Harrison's solution was chosen as the immersion electrolyte due to its ability to imitate an industrial atmospheric environment. At this point in the study, the samples show relatively different responses to the stresses of constant immersion. It is possible to notice visual differences (Figure 2) amongst the Cr-epoxy/polyurethane and POP/polyurethane. It can be seen that the least change and greatest inhibition of blister development occurs in the POP/polyurethane sample. It must be reiterated here that the overall coating thickness of the Cr-Epoxy/polyurethane system is greater than that of the POP/polyurethane systems.

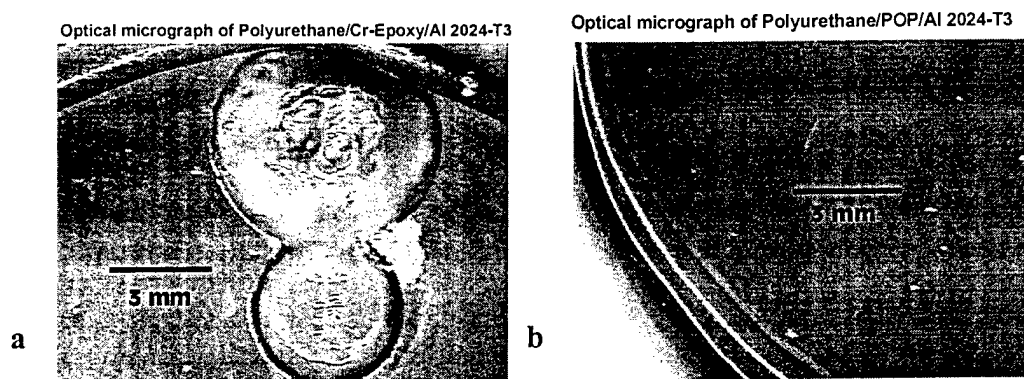


Figure 2. Optical Micrographs of coating systems a) Polyurethane/Cr-Epoxy/Al 2024-T3 and b) Polyurethane/POP/Al 2024-T3.

In addition to visual changes, electrochemical changes were evident by the impedance spectra shown in Figure 3. In Figure 3a, it can be seen that the Polyurethane/Cr-Epoxy/Al 2024-T3 sample had a high impedance at the start of immersion (greater than 10^9 Ohms at 0.01 Hz). Although initially stable, the sample showed drastic failure at 358 days. At the time of failure rather large blisters, over 3 mm in diameter, were evident (Figure 2a). The rapid growth and/or rupture of this blister may be responsible for such a drastic drop in impedance. The Polyurethane/POP/Al 2024-T3 sample continued to maintain the initial impedance value (Figure 3b). The visual appearances of the samples shown in Figure 2 support the EIS results of Figure 3, with the sample exhibiting the smallest visual change (the polyurethane/POP/Al 2024-T3) also displaying the smallest decrease in impedance.

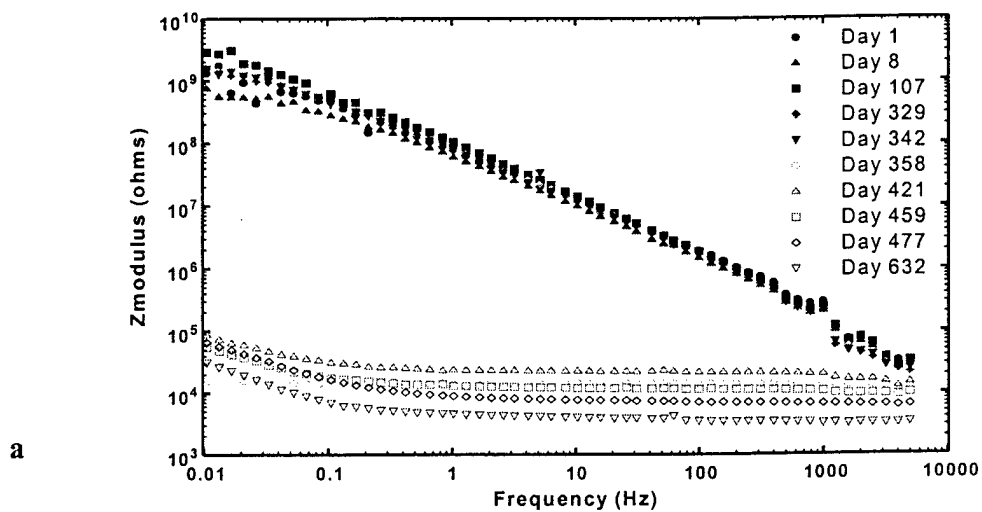
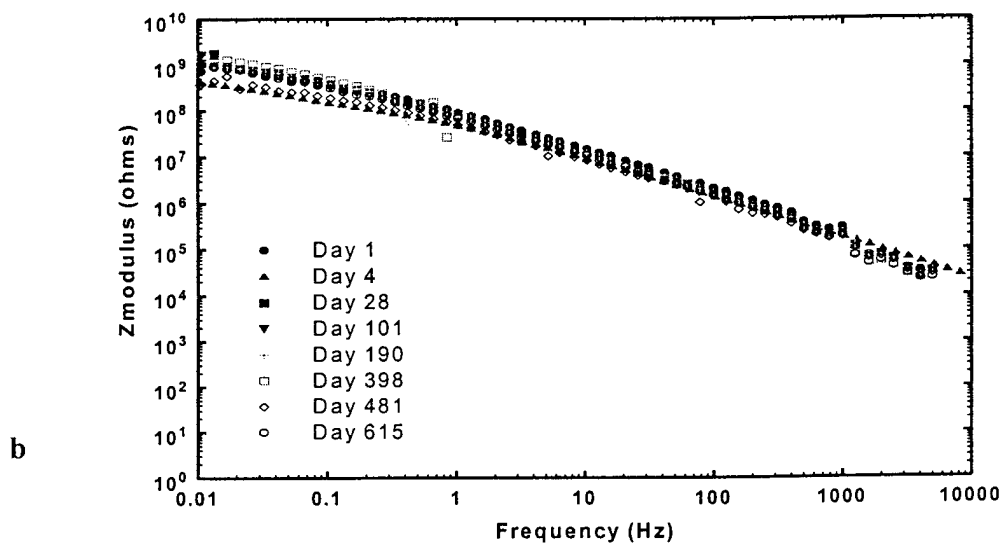
Polyurethane/Cr-Epoxy/Al 2024 T-3**Polyurethane/POP/Al 2024 T-3**

Figure 3. EIS spectra of Coating systems a) Polyurethane/Cr-Epoxy/Al 2024-T3 and b) Polyurethane/POP/Al 2024-T3. (exposed area of ~7 cm²).

Plain-Epoxy on Aluminum and Steel. As a control experiment, current density maps were obtained for steel and Al alloy samples coated with a plain (nonchromated) epoxy primer. A defect was introduced by scribing through the coating to the bare metal surface. The results of these experiments are exemplified by the result for steel shown in Figure 4. Clearly visible in the micrograph of Figure 4 is the 2-mm by 2-mm scan area defined by the Polyester 5 adhesive tape. The defect, which is parallel to the X-axis, is visible within this scan area. From Figure 4, it is clear that the major current flow is from a single anodic site to a single cathodic site, each located within the defect. This confirms that the coating is effectively removed by scribing, exposing the bare metal. In every such control experiment for steel and aluminum, similar behavior was observed, with oxidation and reduction currents confined to the defect. With steel, the onset of corrosion within the defect was very rapid, typically observed in the first scan (i.e., within 5 min.). With aluminum, the onset of corrosion within the defect was somewhat more variable, but was typically observed by the second scan (i.e., within 20 min.). For the steel sample of Figure 4, the current slowly diminished toward zero over the course of approximately 3.5 hours, at which point the leftmost two-thirds of the defect area was covered with corrosion product. The cathodic site remained free of corrosion product throughout the experiment.

Chromated-Epoxy Primer on Steel. Two differences were observed in the experiments involving chromated-epoxy primer on steel. First, whereas large currents were observed within 5-minutes in the control experiments, there was a significant delay of 40-minutes or longer before the onset of any observable corrosion current in these experiments. Second, significant reduction current on the exposed metal in the defect, as always observed in the control experiments, was not observed in these experiments.

Figure 5 shows a sample after 169-minutes of immersion (the first observable current for this particular sample was at 42-minutes immersion). Oxidation was clearly occurring within the defect and corrosion product is visible at the anodic site in the optical micrograph. However, little if any reduction occurred within the defect. Rather, reduction appeared to occur more or less uniformly across the coating surface. Since the reduction current was spread out over a relatively large area, the current density at any one point was rather small, similar in magnitude to the noise level. Therefore, we repeated this experiment eight times to confirm this general behavior. In every case the surface of the coating was uniformly depressed below zero current (i.e., uniformly cathodic), with little or no reduction current within the defect. With the plain epoxy control experiments, the total anodic current and total cathodic current flowing above the defect were approximately equal. In these chromated-epoxy experiments, the anodic current was always greater. We conclude that reduction in these experiments did indeed occur over the chromated-epoxy coating. In these experiments, we observed no tendency for the chromated-epoxy primer to rapidly passivate the steel. In fact, once corrosion current began to flow (following the initial delay), it continued for 18 to 20 hours, until corrosion products eventually covered the

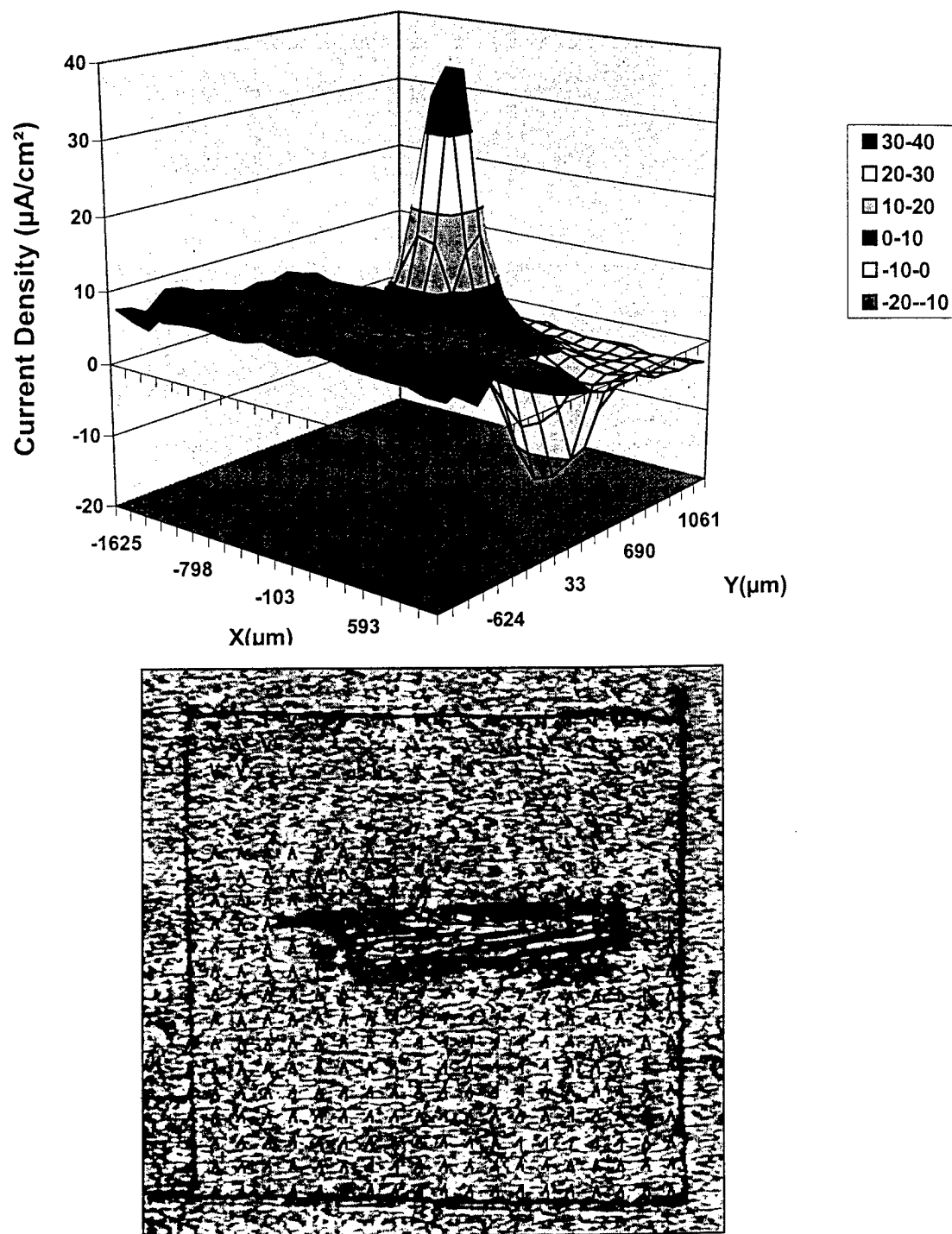


Figure 4. Current density maps for the plain epoxy primer on steel at 5 minutes immersion in 3% NaCl: (top) 3D representation of the z component of the current density and (bottom) optical micrograph of the sample with current density vectors superimposed.

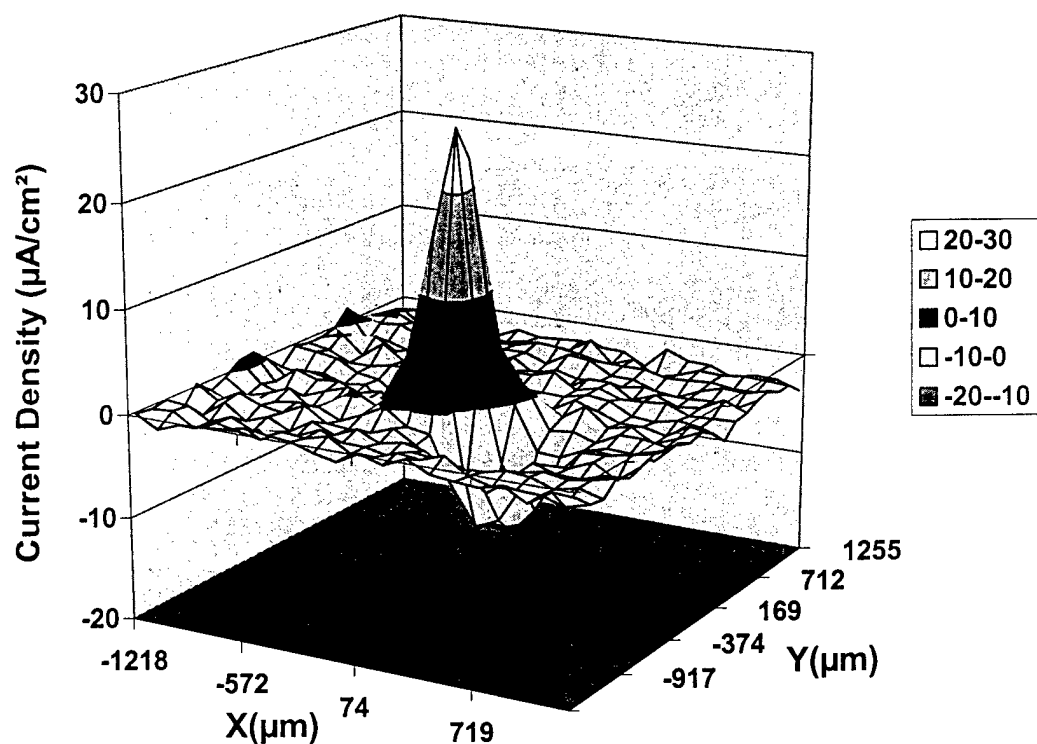


Figure 5. Current density maps for the chromated-epoxy primer on steel at 169 minutes immersion in 3% NaCl: (top) 3D representation of the z component of the current density and (bottom) optical micrograph of the sample with current density vectors superimposed.

Chromated-Epoxy Primer on Al 2024-T3. The chromated-epoxy primer on Al 2024-T3 alloy, as on steel, significantly retarded the onset of corrosion. Whereas corrosion activity was observed within ca. 20 min. for the plain epoxy control samples, the first detectable current with the chromated-epoxy samples was typically after 5-hours of immersion. The results are exemplified by Figure 6, which shows the current density maps for a particular sample after 5-minutes immersion and after 5.5-hours immersion. The 5-minute map is typical of those obtained over the first 5-hours of immersion, showing no detectable corrosion of the metal exposed in the defect. The exposed metal in the defect remained shiny during this period. The first sign of corrosion is displayed in the 5.5-hour map (Figure 6), with both oxidation and reduction being confined to the defect area. As with the steel samples, this corrosion current continued to increase over the next several hours of immersion, and most of the exposed metal area in the defect turned dark in color. Figure 7 shows the current density maps for the same sample after 17.5-hours immersion, by which time the current had increased substantially but still appeared to be confined to the defect area. Two local cathode sites, one on each side of the anode site, are observed. As noted in the previous section, this behavior is in contrast to that on steel where cathodic currents above the coating were observed. The site of corrosion is clearly visible in Figure 7 as the remaining shiny metal spot in the micrograph.

Poly(3-octyl pyrrole) Coating on Steel. There are rather striking similarities between the results obtained in this work with the POP coating on steel and the results reported for a chromated-epoxy coating on steel. As was observed with the chromated-epoxy coating, the POP coating delayed the onset of corrosion within the defect. However, the delay was significantly longer, typically ca. 3 hours with the POP coating, compared to ca. 40 minutes for the chromated epoxy coating and virtually no delay for a plain epoxy coating. Figure 8 (top) shows the current density map for POP-coated steel at 5-minutes immersion in 3% NaCl (the optical micrograph for this sample is displayed in Figure 9). No significant current flow was observed and similar inactivity was maintained for ca. 3 hours. Figure 8 (bottom) shows the map recorded at 166-minutes immersion, at which time the first significant current flow was observed. The current increased with time, reaching the maximum (ca. $100 \mu\text{A}/\text{cm}^2$) after 5-hours and 35-minutes immersion (Figure 9). The current then slowly decreased as the defect became covered with a dark deposit of corrosion product, reaching near background levels after ca. 19 hours. As observed for a chromated epoxy coating (but in contrast to a plain epoxy coating), the corrosion product appeared to be adherent, with little or no suspended corrosion product evident in the immersion solution.

In these experiments, the current associated with the defect is always anodic, with two main anodic sites for this particular sample apparent in the current maps of Figure 9. Significant cathodic current was never observed within the defect. Rather, the cathodic current was always distributed more or less uniformly across the conducting polymer surface, as clearly evident from Figure 9. We postulate that oxygen reduction occurs at the POP/electrolyte interface, with electron transfer from the metal to oxygen being mediated by the POP. This process drives the oxidation reaction observed in the defect, which ultimately leads to passivation of the exposed metal within the defect. Of course, the oxidizing potential of POP may be an important factor in this mediation process.

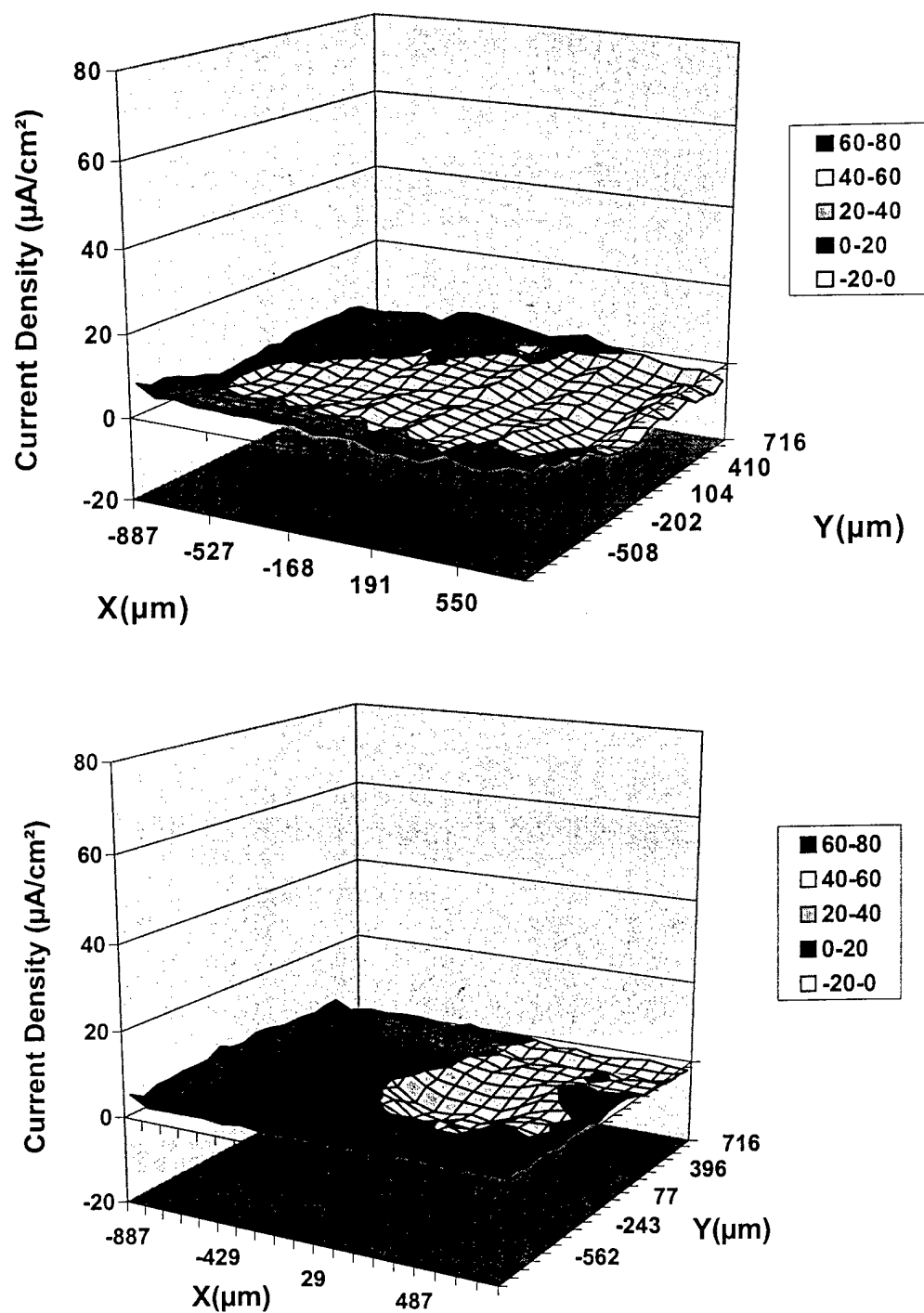


Figure 6. Current density maps for the chromated-epoxy primer on Al 2024-T3 at (top) 5 minutes and (bottom) 5.5 hour immersion in dilute Harrison's solution (3D representation of the z component of the current density).

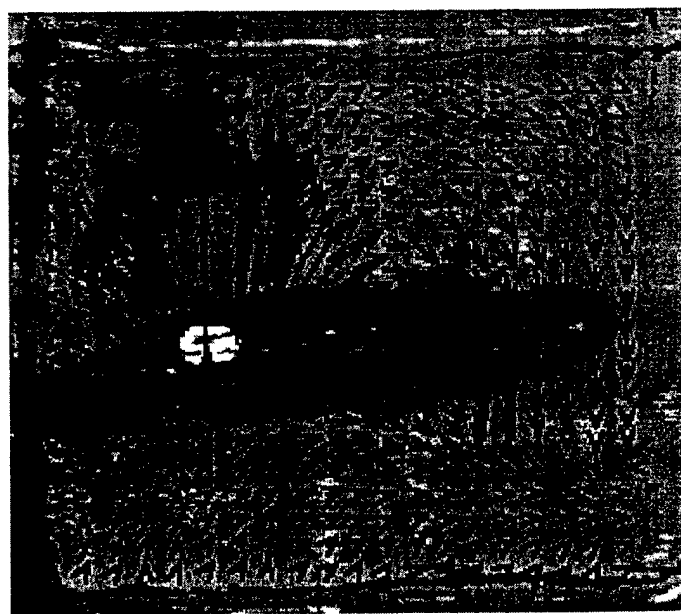
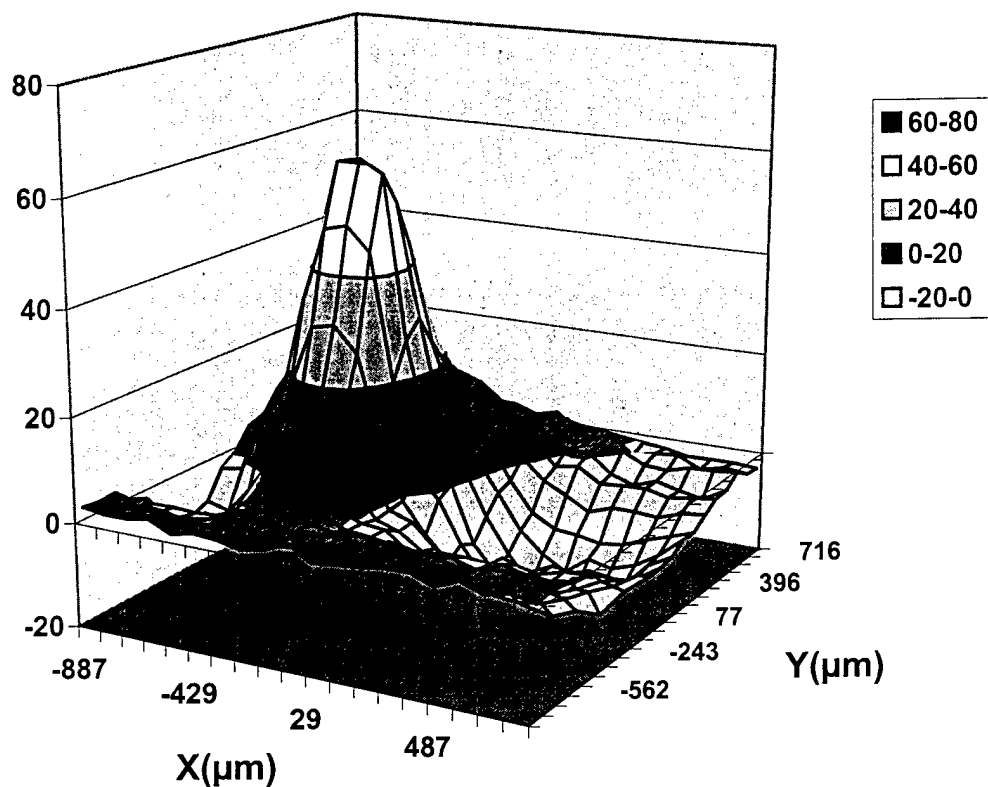


Figure 7. Current density maps for the chromated-epoxy primer on Al 2024-T3 at 17.5 hours immersion in dilute Harrison's solution: (top) 3D representation of the z component of the current density and (bottom) optical micrograph of the sample with current density vectors superimposed.

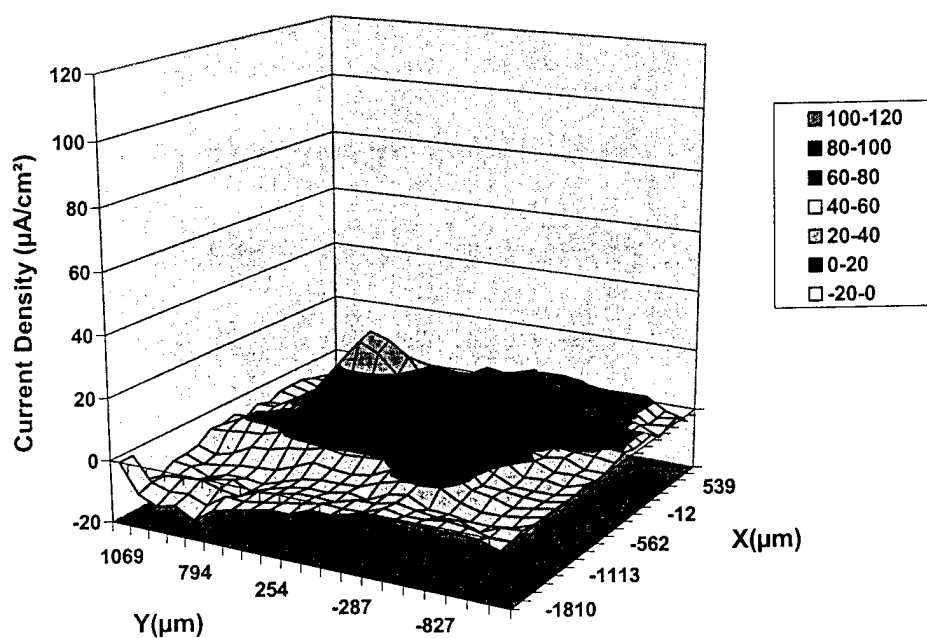
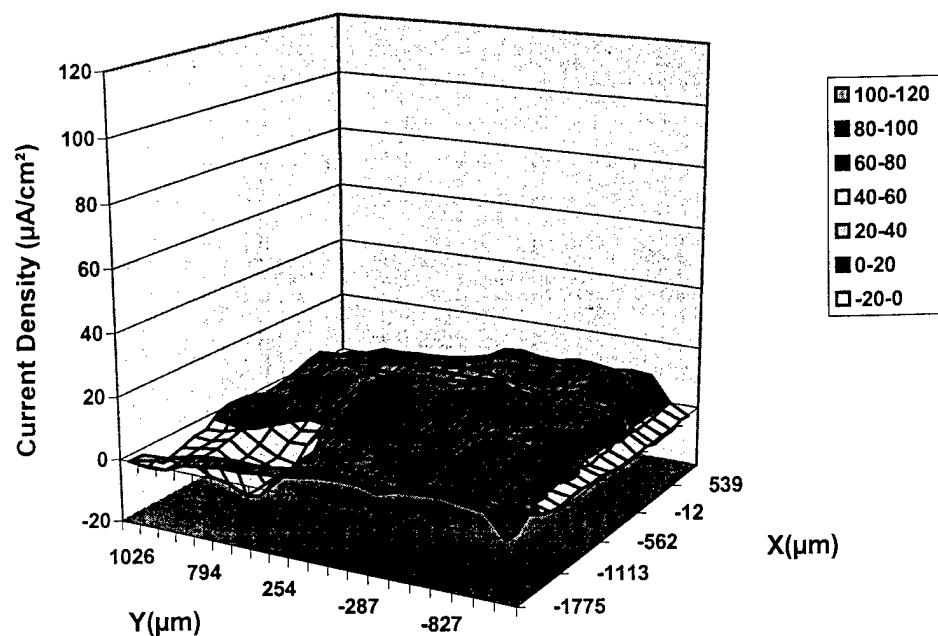


Figure 8. Current density maps for POP on steel in 3% NaCl at (top) 5 minutes and (bottom) 2 hours and 46 minutes immersion (3D representation of the z component of the current density).

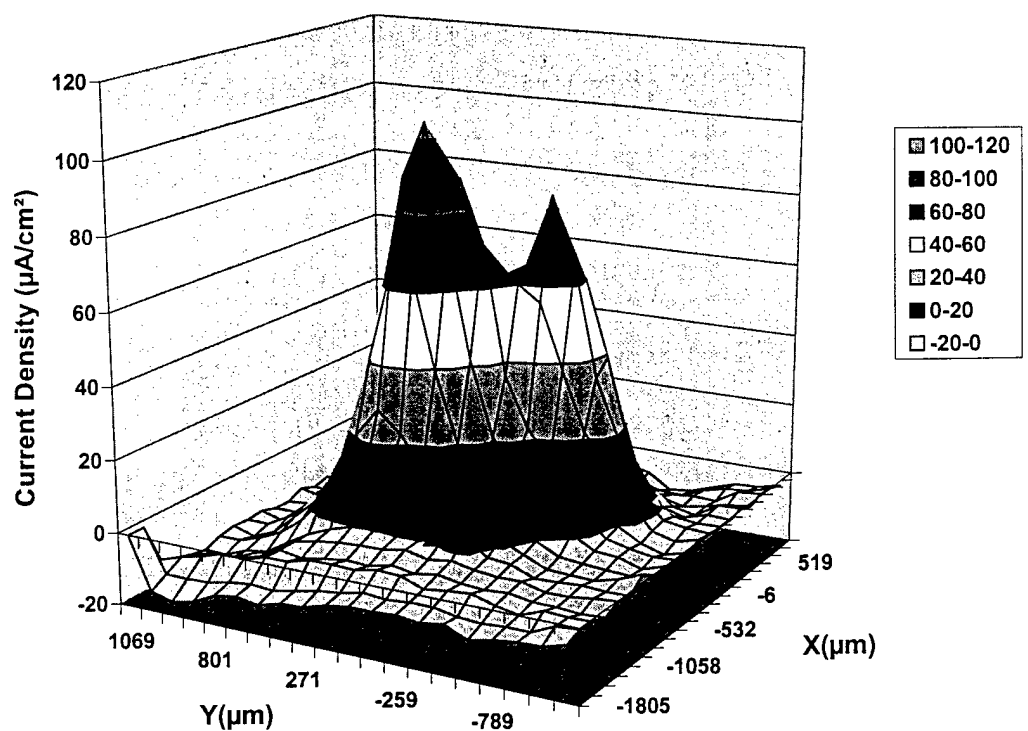


Figure 9. Current density maps for POP on steel at 5 hours 35 minutes immersion in 3% NaCl: (top) 3D representation of the z component of the current density and (bottom) optical micrograph of the sample with current density vectors superimposed.

Poly(3-octyl pyrrole) Coating on Al 2024-T3. The results obtained for POP on Al 2024-T3 are particularly interesting. In the initial experiments, the defects introduced into the coatings were of dimensions similar to those used for the steel samples (for example, see Figure 9). However, little or no activity was observed with these samples even after many hours of immersion, so the size of the defect was increased. Figure 10 illustrates a typical sample with the larger defect, this optical micrograph and current density map captured at the 5-minute mark. Close examination of the current density map reveals a very small oxidation current flowing at the defect, particularly noticeable at the left edge of the defect, corresponding to the left end of the X-axis and the midpoint of the Y-axis. A correspondingly small reduction current occurs at coated areas of the substrate. Admittedly these currents are near the background level, but may reflect the development of a protective oxide coating at the defect during the early stages of immersion. Even with this rather sizable defect, the current flow typically remained at near background level for over 22 hours. By comparison, sizable current flow ($>10 \mu\text{A}/\text{cm}^2$) was observed at chromated-epoxy coatings within ca. 5 hours and at plain epoxy coatings within ca. 20 minutes.

The first significant current flow at this sample was observed after 22-hours, 14-minutes of immersion, shown in Figure 11 (top). However, in contrast to other combinations of coatings and metals we have examined where oxidation always occurred at the defect, the oxidation current in this case appeared to originate at a coated area of the aluminum alloy. The current increased over the next hour during which time the defect area exhibited a rather uniform reduction current (Figure 11). Indeed, from this time of immersion onward, oxidation at the defect was never observed with these samples. The metal within the defect remained shiny throughout the immersion experiment with no visual evidence of corrosion products. To assess the reproducibility of this observation, a total of eight POP-coated samples were examined by the SVET. In every case, the above general behavior was observed, with no significant oxidation occurring at the defect of any of the eight samples. Additionally, there appeared to be no coating defects (e.g., pinholes) that might account for the observed behavior. The oxidation currents observed in Figure 11 indicate that anions were moving into (or equivalently, cations out of) the POP coating.

There remains a confounding question. Why does the oxidation of aluminum alloy always occur under the polymer coating and not at exposed metal within the defect as observed for steel? After all, the defect area is exposed directly to the aggressive electrolyte ions, whereas the POP-coated area is not (although exchange of the POP counterions with electrolyte ions likely occurs). One explanation might involve direct oxidation of the metal by the POP with concomitant reduction of the POP. However, such an internal redox reaction would not require charge compensation of the POP from the electrolyte (i.e., there would be no ion flux at the POP surface) and such a process would not be observed by the SVET. The POP coating may mediate the oxidation of the alloy by shuttling electrons from the alloy to oxygen (or other oxidant) at the POP/electrolyte interface, as observed for steel (Figure 9). Indeed, reduction at the POP/electrolyte interface (as well as in the defect) was often observed with the Al alloy. However, the mediation of electron transfer by the POP would not explain the absence of oxidation within the defect and the localized undercoating oxidation.

One possible explanation is that the POP provided a thermodynamic assist to the oxidation of the aluminum alloy by forming stable metal ion complexes with the oxidized metal ions (principally Al^{3+} and/or Cu^{2+}). Indeed, a similar mechanism has been suggested for polyaniline on Al 2024-T3, where X-ray photoelectron spectroscopy showed depletion of Cu

from the alloy surface by the conducting polymer.ⁱⁱ As the metal ions enter the POP, charge balance would be maintained by an anion flux from electrolyte into the polymer, resulting in the observed current flow above the polymer surface. A slight color change in the POP coating immediately above and around the site of oxidation was observed (from black to dark blue-green), indicating a localized change in coating composition consistent with this hypothesis. Furthermore, the incorporation of metal ions into polypyrrole by complexation has been reported, both by direct coordination to the pyrrole nitrogenⁱⁱⁱ and by incorporation and strong binding (as counterions) of anionic metal complexes.^{iv}

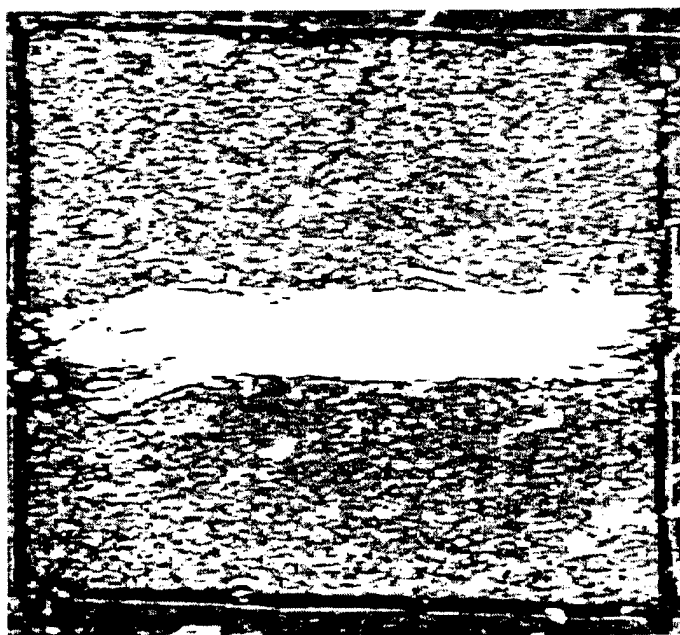
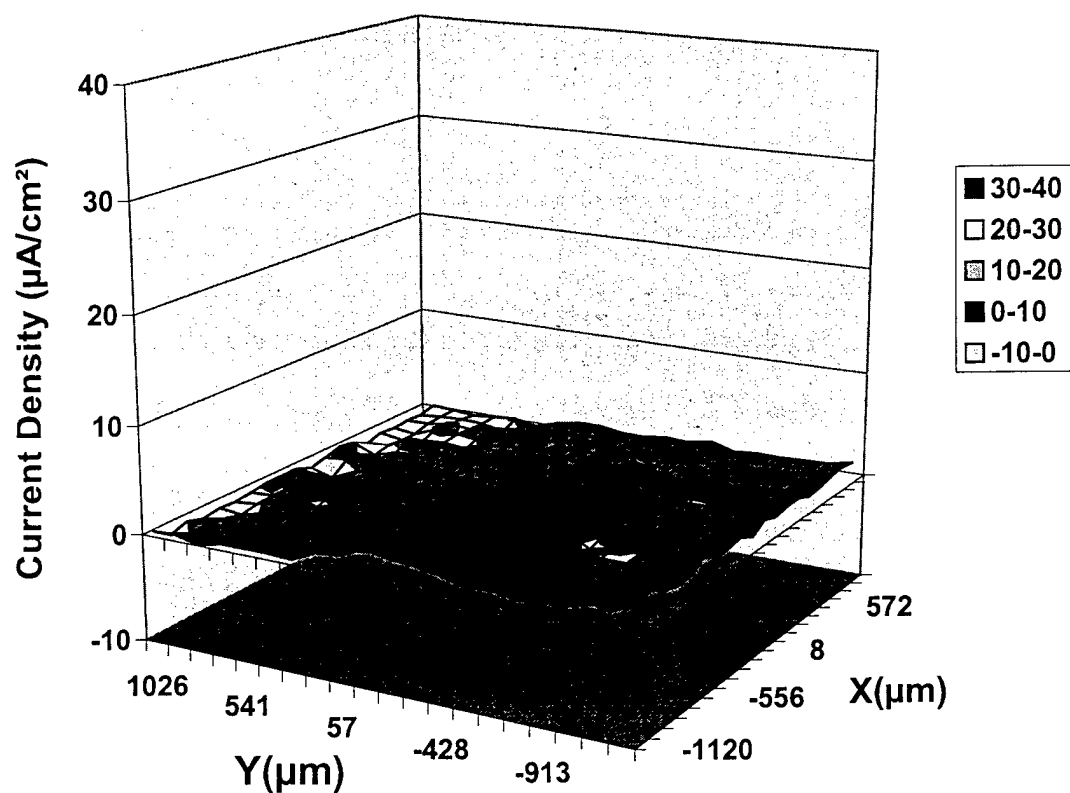


Figure 10. Current density maps for POP on Al 2024-T3 at 5 minutes immersion in dilute Harrison's solution: (top) 3D representation of the z component of the current density and (bottom) optical micrograph of the sample with current density vectors superimposed.

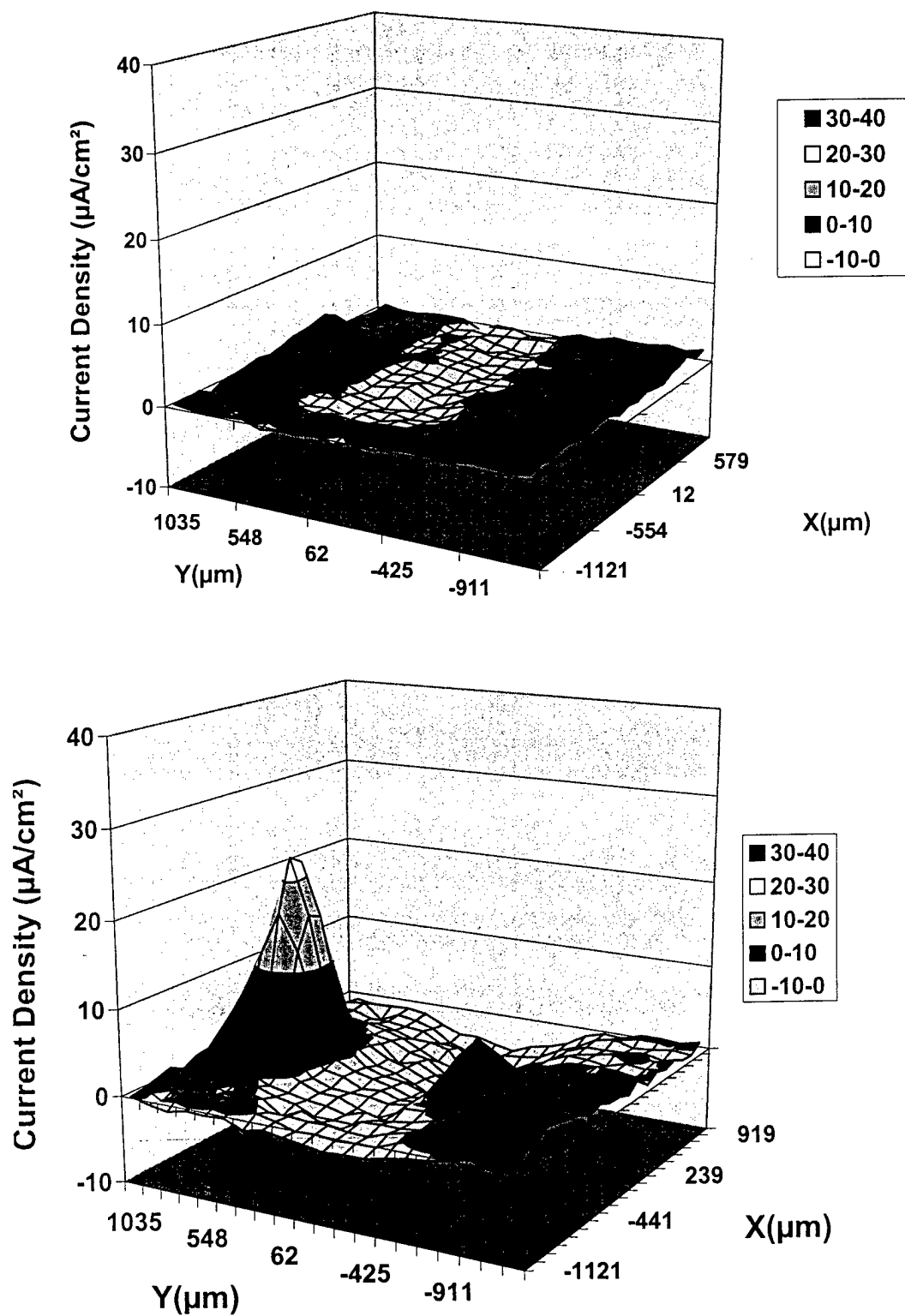


Figure 11. Current density maps for POP on Al 2024-T3 in dilute Harrison's solution at (top) 22 hours and (bottom) 23 hours and 14 minutes immersion (3D representation of the z component of the current density).

SUMMARY AND CONCLUSIONS

Poly(3-octyl pyrrole) coatings on cold-rolled steel and on aluminum 2024-T3 alloy have the ability to delay the onset of corrosion within a defect. In this regard, the POP coatings are similar to chromated-epoxy coatings, but produce even longer delays before the onset of current flow in and around the defect. The defect apparently is protected by a mechanism involving formation and/or stabilization of a passive layer in the defect, likely a consequence of the ability of these coatings to render the surface potential within the defect more positive (noble). Eventually, however, the aggressive immersion medium breaches the passive layer and corrosion commences.

The chromated-epoxy coating delayed the onset of corrosion of both the steel and aluminum substrates compared to a plain epoxy coating. Apparently the chromated-epoxy coating initially promoted formation and/or stabilization of a passive layer within the defect region, slowing the corrosion process. However, the aggressive immersion conditions eventually led to a breach of this passive layer and corrosion current began to flow. Cathodic inhibition by CrO_4^{2-} may also play a role during this initial delay period. It should be noted that the SVET detects only those reactions that involve one or more ionic species. If a reaction such as $\text{M} + \text{O}_2 \rightarrow \text{MO}_2$ occurred, there would be no attendant ion flux in the electrolyte and such a reaction would not be detected by the SVET. Thus, it is possible (though rather unlikely in view of the control experiments) that such a corrosion process occurred during this apparently inactive delay period.

Once detectable corrosion commenced, the chromated-epoxy coating actually appeared to sustain the current at both metals for a longer period of time than observed with the plain epoxy coating. That is, the time to passivation of both metals, as determined by the decrease in measured anodic current within the defect, was longer with the chromated-epoxy coating than with the plain epoxy coating. This surprising observation may be an important aspect of the long-term protection mechanism of chromate-based coatings, leading to passive films of different composition and perhaps more resilience than that produced in the absence of chromate.

Further details of these (and related) studies may be found in the following publications:

D.E. Tallman, Y. Pae, G. Chen, G.P. Bierwagen, B. Reems, and V. Gelling, "Studies of Electronically Conducting Polymers for Corrosion Inhibition of Aluminum and Steel," Annual Technical Conference - Society of Plastic Engineers (ANTEC '98) 56(2) (1998) 1234-1237.

D.E. Tallman, Y. Pae and G.P. Bierwagen, "Conducting Polymers and Corrosion: Part 2 - Polyaniline on Aluminum Alloys," Corrosion 56 (2000) 401-410.

J. He, V. Johnston-Gelling, D.E. Tallman, and G.P. Bierwagen, "A Scanning Vibrating Electrode Study of Chromated Epoxy Primer on Steel and Aluminum," J. Electrochem. Soc. 147 (2000) 3661-3666.

J. He, V. Johnston-Gelling, D.E. Tallman, G.P. Bierwagen, and G.G. Wallace, "Conducting Polymers and Corrosion 3: A Scanning Vibrating Electrode Study of Poly(3-Octyl Pyrrole) on Steel and Aluminum," J. Electrochem. Soc. 147 (2000) 3667-3672.

J. He, V. Johnston-Gelling, D.E. Tallman and G.P. Bierwagen, "A Scanning Vibrating Electrode Study of Chromated-Epoxy Coatings on Steel and Aluminum," *Polymer Preprints*, 41 (2000) 1755-1756.

J. He, V. Johnston-Gelling, D.E. Tallman and G.P. Bierwagen, "Scanning Vibrating Electrode Study of Electronically Conducting Polymers on Aluminum Alloy," *Polymer Preprints*, 41 (2000) 1774-1775.

V. Johnston-Gelling, D.E. Tallman, G.P. Bierwagen and G.G. Wallace, "Study of Poly(3-Octyl Pyrrole) for Corrosion Control of Aluminum 2024-T3," *Polymer Preprints*, 41 (2000) 1770-1771.

V. Johnston-Gelling, M.M. Wiest, D.E. Tallman, G.P. Bierwagen and G.G. Wallace, "Electroactive Conducting Polymers for Corrosion Control: Studies of Poly(3-Octyl Pyrrole) and Poly(3-Octadecyl Pyrrole) on Aluminum 2024-T3 Alloy," *Prog. Organic Coatings* (2001) in press.

ACKNOWLEDGEMENTS

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- ii. A. J. Epstein, J. A. O. Smallfield, H. Guan and M. Fahlman, *Synthetic Metals*, **102**, 1374 (1999).
- iii. M. B. Inoue, K. W. Nebesny, Q. Fernando, Ma. M. Castillo-Ortega and M. Inoue, *Synthetic Metals*, **38**, 205 (1990).
- iv. A. Deronzier and J-C. Moutet, *Coordination Chemistry Reviews*, **147**, 339 (1996).

**Contribution of
Prof. M.W. Urban, Prof. S. G. Croll
Department of Polymers and Coatings**

Summary of Research Activities and Results FY 1997 through FY 2000

Major Accomplishments

Detailed in section below.

Equipment Additions

FTIR Microscope. 1997 Model Microscope from Nicolet.

Controller for Raman Microscope. From Bruker in 1996.

Laser for Raman Microscopy. From Quality Electro-optical Devices

Raman chemical imaging microscope upgrade to Olympus BH series microscope, ChemIcon, Inc.

Computers/Electronics. Multiple computers and small electronics/equipment have also been added.

Personnel Contributing to this Study

S. G. Croll PI, M. W. Urban PI, K. Katti post-doctoral associate, C.K. Vang, B. Kiland graduate student, H. Kim post-doctoral associate

Publications:

Hueng Kim and Marek W. Urban, "Molecular Level Chain Scission Mechanisms of Epoxy and Urethane Polymeric Films Exposed to UV/H₂O. Multidimensional Spectroscopic Studies", *Langmuir* 2000, 16, 5382-5390

C. Vang, J.P. Li, S. Croll, G.P. Bierwagen and D.E. Tallman, "Chemical Degradation of a Self-Priming (Unicoat) Polyurethane Protective Aircraft Coating Exposed to Two Accelerated Weathering Exposures: I. An FTIR Spectroscopy Approach.", *Journal of Polymer Degradation and Stability* (in review)

C. Vang, J.P. Li, S. Croll, G.P. Bierwagen and D.E. Tallman, "Chemical Degradation of a High Gloss Polyurethane Protective Aircraft Coating Exposed to Two Accelerated Weathering Exposures: II. An FTIR Spectroscopy Approach.", *Journal of Polymer Degradation and Stability* (in review)

C. Vang, J.P. Li, S. Croll, G.P. Bierwagen
and D.E. Tallman, "Chemical Degradation of a Fluorinated Polyurethane Protective Aircraft
Coating Exposed to Accelerated Weathering Exposure: III. An FTIR Spectroscopy Approach",
Journal of Polymer Degradation and Stability (in review)

Presentations at Technical Meetings:

1. Hau, Q; Urban M.W.; Proc. PMSE, Vol 82, 2000, 384.
2. Ralpano Ratti; M.W. Urban; Proc. PMSE, Vol 85, 2001, 107.

Chemical Degradation of Polyurethane Protective Aircraft Coatings Exposed to Accelerated Weathering Exposures: Chemical Pathways and Spectroscopic Studies.

C. Vang, S.G. Croll¹, and G.P. Bierwagen¹, co-PIs¹

Abstract. Linear and step-scan photo acoustic Fourier transformed infrared (FT-IR) spectroscopy, FT-IR microscopy, and Raman chemical imaging were utilized to examine molecular level degradation processes in epoxy and polyurethane films. These films included a self-priming (Unicoat), high gloss and fluorinated polyurethane aircraft coatings. Accelerated weathering protocols used were QUV/H₂O and the combined QUV/H₂O and Prohesion[®] weathering (which simulates acid rain) exposure. A combination of the measurement techniques allowed us to determine a three-dimensional representation of degradation processes and showed that the extent of cross-linking in epoxy films varies as a function of depth from the surface. When exposed to 340 nm ultraviolet (UV) radiation and water vapor condensation, epoxy films degrade to form cracks, whose surfaces are composed of primary amines and resulted from a chain scission of the C-N bonds in cross-linked bisphenol A epoxy films. Polyurethane films exhibit the presence of two surface domains, which are composed of polyurethane- and polyurea-rich regions. When exposed to 340 nm UV radiation and water vapor condensation, polyurea is converted to polyurethane entities. Mechanisms leading to these processes are proposed and indicated which isocyanate and polyol reactions occur in the presence of H₂O and UV light. Compared to other aircraft urethane coating systems, the fluorinated material degraded slower, which shows the importance of formulation and chemical structure, even within the same class of materials.

Conclusions. Chemical structural changes occur during accelerated QUV/H₂O and the combined QUV/H₂O and Prohesion[®] weathering (which simulates acid rain) exposure in polyurethane aircraft coatings. The QUV/H₂O and Prohesion[®] exposure test condition combines the synergistic effects of UV light, electrolyte, moisture, and temperature in its cycle, which simulates the damaging effects caused by the aggressive natural exposure environment conditions. The QUV exposures utilize fluorescent light sources (UV-A bulb at 300-380 nm) that emit UV wavelengths higher in energy than most of those found in natural sunlight. Accelerated degradation studies are particularly useful, if molecular level information can be related to macroscopic observations on well-defined polymeric systems. This fundamental understanding allows for more representative accelerated weathering testing along with intelligent design of more durable coatings.

A combination of linear and step-scan photoacoustic (PA) Fourier transformed infrared (FT-IR) spectroscopy, FT-IR microscopy, and Raman chemical imaging were utilized in an effort to obtain a three-dimensional representation of degradation mechanisms. While surface morphologies of epoxy and polyurethane films can be analyzed using FT-IR microscopy and Raman chemical imaging, step-scan PA FT-IR spectroscopy allowed us to examine degradation processes deeper into both the epoxy and polyurethane bulk material. Thus, using these approaches we were able to elucidate molecular level stratification processes in epoxy and polyurethane films and their localized nonhomogeneous molecular level degradation resulting from UV exposure in the presence of H₂O vapor. The issue is how to detect molecular level

degradation processes occurring, not only on polymeric film surfaces but also as a function of depth from the surface, and be able to correlate molecular level processes resulting from degradation to macroscopic changes. After all, when photochemical reactions occur, chemical entities resulting from these reactions will alter numerous surface properties. In view of the above, this study focused on degradation mechanisms of epoxy and polyurethane as well as the use of molecular level probes for studying their degradation. A summary of major results is given below.

- 1) When epoxies are exposed to UV radiation, scission occurs between carbon and nitrogen atoms, and amine groups are produced due to high reactivity of nitrogen-terminated radicals. Mechanisms of polyurethane degradation exposed to UV radiation were proposed and it was seen that urethane C-N and N-H linkages, which react with hydrogen or oxygen from the atmosphere, are responsible for network degradation.
- 2) A) These studies show that bisphenol A epoxy is uniformly distributed across the film thickness, but a higher degree of cross-linking reactions of bisphenol A oxirane groups occurs at greater depths from the surface. Therefore, a greater amount of OH functionalities exists further away from the surface. When such specimens are exposed to 340 nm wavelength UV radiation and water vapor condensation, epoxy films degrade to form cracks whose surface is composed of carbonyl amides due to chain scission.
B) Concurrent studies conducted on high gloss polyurethane show that an excessive amount of polyurea due to cross-linking reactions of polyurethane-NH and HDI-NCO groups exists at shallower depths from the surface and form heterogeneous domains on the surface. Upon UV radiation and water vapor treatment, polyurea converts to polyurethane, thus ultimately extending UV/H₂O durability. These studies also show that step-scan PA FT-IR, IR microscope, and Raman chemical imaging are powerful tools for analyzing molecular level degradation processes occurring in epoxy and polyurethane polymer films in three dimensions.
- 3) Spectroscopic results on self-priming (Unicoat) polyurethane aircraft coating indicated that the QUV-water vapor condensation exposure condition had a greater effect on the overall coating degradation. After 20 weeks of exposure, an increase of polyurethane components was found at film-air surfaces, whereas a reduction of polyurethane-urea band intensity (1690 cm^{-1}) was detected. In addition, the formation of hydrogen-bonded carbonyl moieties was also present. In the combined accelerated QUV-water vapor condensation and salt spray (Prohesion[®]) exposure conditions, there was no detectable hydrogen bonded urethane components on film-air surfaces. However, as coating depth increases, detectable hydrogen-bonded urethane crosslinks were observed. Result plots illustrated that during the combined cyclic weathering exposure, degradation of the polyurethane coating was minimal. In fact, spectroscopic results of the relative carbonyl intensities at 1728 , 1710 , and 1690 cm^{-1} of the coating remained the same to the end of 18 weeks exposure. Chemical oxidation on coating surfaces that leads to coating degradation was also observed by the reduction of coating gloss and contact angle measurements.
- 4) Spectroscopic studies on high gloss polyurethane coating indicated that the QUV-water vapor condensation exposure condition had a greater effect on the overall coating degradation. After 20 weeks of exposure, an increase of polyurethane components was found at film-air surfaces, whereas a reduction of polyurethane-urea band intensity (1690

cm^{-1}) was detected. In addition, the formation of hydrogen-bonded carbonyl moieties was also present. In the combined accelerated QUV-water vapor condensation and salt spray (Prohesion[®]) exposure conditions, there was no detectable hydrogen bonded urethane components on film-air surfaces. However, as coating depth increases, detectable hydrogen-bonded urethane crosslinks were observed. Result plots illustrated that during the combined cyclic weathering exposure, degradation of the polyurethane coating was minimal. In fact, spectroscopic results of the relative carbonyl intensities at 1728, 1710, and 1690 cm^{-1} of the coating remained the same to the end of 18 weeks exposure. Chemical oxidation on coating surfaces that leads to coating degradation was also observed by the reduction of coating gloss and contact angle measurements. Compared to the Unicoat urethane coating system, this gloss material degraded slower, which shows the importance of formulation and chemical structure, even within the same class of materials. . Although, both the high gloss and self-priming polyurethane coatings show a decreasing trend with respect to both coating gloss and contact angle measurements, the high gloss polyurethane coating appears to degrade more slowly than the self-priming urethane system.

- 5) Exposure of the fluorinated polyurethane coating to prolong periods of extreme weathering conditions (day 0 to week 59) indicated a loss of both polyurethane/polyurea components at film-air surfaces, which have lead to an increase of disordered hydrogen bonding formations. The slight increase of the 1690 cm^{-1} and 1540 cm^{-1} vibrational bands at longer exposure time further supports the presence of secondary amine groups which therefore enhanced the hydrogen bonded polyurethane-urea R-NH components. Contact angle measurements indicated that as exposure time increases an increase in contact angle measurements was observed. This increase in contact angle measurement is attributed to the presence of fluorinated hydrocarbon species left behind after the chemical deterioration of aliphatic hydrocarbon components. Therefore, both FTIR spectroscopic and contact angle results concluded that although chemical degradation has taken place, the overall integrity of the coating still remains. The fluorinated system chemistry changes more slowly in these exposure conditions than the other urethanes that have been tested.

Details of the studies and results are readily accessible in the published (or to be published) peer reviewed journal articles listed below.

Publications:

Hueng Kim and Marek W. Urban, "Molecular Level Chain Scission Mechanisms of Epoxy and Urethane Polymeric Films Exposed to UV/H₂O. Multidimensional Spectroscopic Studies", *Langmuir* 2000, 16, 5382-5390

C. Vang, J.P. Li, S. Croll, G.P. Bierwagen and D.E. Tallman, "Chemical Degradation of a Self-Priming (Unicoat) Polyurethane Protective Aircraft Coating Exposed to Two Accelerated Weathering Exposures: I. An FTIR Spectroscopy Approach.", *Journal of Polymer Degradation and Stability* (in review)

C. Vang, J.P. Li, S. Croll, G.P. Bierwagen and D.E. Tallman, "Chemical Degradation of a High

Gloss Polyurethane Protective Aircraft Coating Exposed to Two Accelerated Weathering Exposures: II. An FTIR Spectroscopy Approach.", *Journal of Polymer Degradation and Stability* (in review)

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and D.E. Tallman, "Chemical Degradation of a Fluorinated Polyurethane Protective Aircraft Coating Exposed to Accelerated Weathering Exposure: III. An FTIR Spectroscopy Approach", *Journal of Polymer Degradation and Stability* (in review)

**Contribution of
Prof. D. C. Farden
Department of Electrical Engineering**

Summary of Research Activities and Results FY 1997 through FY 2000

Major Accomplishments

Detailed in section below.

Equipment Additions

Gateway computer. Computer for data analysis

Hewlett Packard Oscilloscope. Oscilloscope for instrumentation studies

Computers/Electronics. Multiple computers and small electronics have also been added.

Personnel Contributing to this Study

D. C. Farden PI, G. Meremontes visiting Prof., C. Ophoven undergraduate student, B. Garry graduate student, Stoenescu undergraduate student, D. Banerjee graduate student, J. Datta graduate student

Publications:

G. Miramontes de León, D.C. Farden, and D. E. Tallman,
"Transient Analysis and Simulation of Pitting Corrosion for the Estimation of the Noise Resistance," *Corrosion*, pp. 928-934, September 2000.

Presentations at Technical Meetings:

D. C. Farden, G. Miramontes de León, and D. E. Tallman,
"DSP-Based Instrumentation for Electrochemical Impedance Spectroscopy," *Proceedings 195th Society Meeting of the Electrochemical Society*, Volume 99-5, 98-108 Seattle, Washington, May 2-6, 1999.

D. C. Farden and G. Miramontes de León, "EIS Frequency Response Extrapolation using Parametric Modeling," *presented at the 197th Meeting of The Electrochemical Society in Toronto, Canada*, May 14-18, 2000.

G. Miramontes de León and D. C. Farden, "Retrieving Magnitude and Phase from Electrochemical Noise Data Using System Identification Techniques," *presented at the 197th Meeting of The Electrochemical Society in Toronto, Canada*, May 14-18, 2000.

Graduate Thesis

G. Miramontes de León, "Electrochemical Noise and Electrochemical Impedance Instrumentation Studies," *Ph.D. Dissertation*, North Dakota State University, July 2000.

EIS/ENM Instrumentation Studies

D.C. Farden, PI

Abstract

A new multi-frequency DSP-based EIS system has been prototyped. An algorithm for designing phase-optimized signals for use in this instrument has been implemented. A new technique has been developed for the estimation of noise resistance using transient ENM data. Parametric system identification techniques have been applied to both EIS and ENM data, allowing extrapolation of complex impedance over an extended frequency range.

Summary

Objectives of this study include the development of improved instrumentation and data analysis techniques for corrosion measurements. There are two basic experimental setups for corrosion measurements with electrochemical cells, which, for ease of discussion, we will refer to as the EIS and ENM setups.

The EIS (electrochemical impedance spectroscopy) setup involves a single electrochemical cell. An external signal (a voltage for the potentiostatic arrangement, a current for the galvanostatic arrangement) is applied, and the response (current, or voltage) is measured. The goal of the EIS method is to estimate the complex impedance of the electrochemical cell over a range of frequencies. It is well known that the electrical characteristics of an electrochemical cell are non-linear. Common treatment of this issue is to apply a small signal (typically less than 10mV peak-to-peak) to justify a linear approximation. Violation of this condition will make meaningful estimation of impedance difficult, but may well yield useful data for establishing valid models for the electrochemical cell.

The ENM (electrochemical noise method) setup typically involves two nominally identical electrochemical cells. No external signal is applied. Simultaneous voltage and current measurements are made. The goal of the ENM technique is to provide an estimate of the noise resistance $R_n = \sigma_v / \sigma_i$, where σ_v is the standard deviation of the potential, and σ_i is the standard deviation of the current. If the potential and current data are obtained with proper observance of the sampling theorem, then ENM data collected from an ENM setup can be used to estimate complex impedance.

The development of a DSP-based instrument for the simultaneous real-time measurement of the impedance at many frequencies using an optimized imposed signal is presented in [1]. For the implementation of this technique an integrated environment using DSP hardware and software was developed. A gradient-descent type algorithm, rather than phase randomization, has been devised for the design of a multi-frequency signal which has adjusted phases for the individual frequency components to minimize the amplitude of the composite signal. This new imposed signal fully exploits the theoretical properties of the Discrete Fourier Transform (and Discrete Fourier Series), when applied to band-limited signals, improving the accuracy and extending the limits of the instrument. The simultaneous measurement at multiple frequencies can provide a substantial reduction in the time required for acquiring the measurement data.

A novel approach for the measurement of noise resistance based on the transient behavior of pitting corrosion is presented in [2, 5]. Potential noise and current transients have been recognized as a characteristic behavior of pitting corrosion. This new approach uses the transient information present during corrosion as a way to estimate directly the noise resistance of coated metals. Computer simulation and analytical results are presented, indicating that the new technique can be applied to the problem of noise resistance estimation. This new approach was applied to experimental ENM data obtained with commercial EIS/ENM equipment.

Information regarding the very low frequency behavior of an electrochemical cell is of great interest as an indication of coating effectiveness in corrosion studies. Direct measurement of low frequency data using very low excitation levels is very difficult due to instrumentation noise which increases with decreasing frequency. Adding to the problem is the fact that more time is necessary to make such measurements (several cycles of the lowest frequency signal are needed). An alternative [3] is to have an electric circuit model of the system. If the model is indeed a valid model, one may estimate parameters of the model based on whatever data is available. The frequency response of the model may then be examined over whatever frequency range is of interest. An easy example of this approach is when the physical system is accurately modeled by an RC circuit for which measurement data at any two frequencies will suffice. The multi-frequency EIS method [1] is ideally suited to perform such measurements. It is important to point out that such an approach may even be applicable to nonlinear systems provided that an accurate model structure is available.

ENM data has been analyzed using system identification (SI) techniques [4]. Phase information is lost in many common analysis techniques where parameters like the "noise impedance" $Z_n(f)$, is obtained from estimates of the power spectral densities (PSDs) of electrochemical noise, and the "noise resistance" R_n is obtained from estimates of the standard deviations of potential and current noise. By modeling the relationship between the voltage and current data, using parametric system identification techniques, it is possible to obtain smooth magnitude and phase plots from the potential and current noise. Furthermore, the model gives information about the zeros and poles of the system and, possibly, capacitance and resistance values can be obtained.

An overview of most of the above, including a critical literature review is available in [5].

References

- [1] D. C. Farden, G. Miramontes de León, and D. E. Tallman, "DSP-Based Instrumentation for Electrochemical Impedance Spectroscopy," *Proceedings 195th Society Meeting of the Electrochemical Society*, Volume 99-5, 98-108 Seattle, Washington, May 2-6, 1999.
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- [3] D. C. Farden and G. Miramontes de León, "EIS Frequency Response Extrapolation using Parametric Modeling," *presented at the 197th Meeting of The Electrochemical Society in Toronto, Canada, May 14-18, 2000.*
- [4] G. Miramontes de León and D. C. Farden, "Retrieving Magnitude and Phase from Electrochemical Noise Data Using System Identification Techniques," *presented at the 197th Meeting of The Electrochemical Society in Toronto, Canada, May 14-18, 2000.*
- [5] G. Miramontes de León, "Electrochemical Noise and Electrochemical Impedance Instrumentation Studies," *Ph.D. Dissertation, North Dakota State University, July 2000.*

Chapter VI

Extensions of this Work

Due to the success of this program, further funding has been secured by our research group to continue our efforts in combating the corrosion of aircraft alloys. The research has been extended due to a grant from AFOSR entitled "Corrosion Protection of Aluminum Alloys Used in Aircraft", with support extended to 2002. Research is being conducted in the areas of a) improved electrochemical, spectral and optical test methods and protocols, including new instrumentation and methods, for characterization the performance of coated aircraft alloys, b) development of molecular probes for examining changes in thin coating films during exposure, c) new metal chrome-free pretreatments materials based on sol-gel optimization, d) further examination of conductive polymers for chrome-free metal pretreatments/primers for Al alloys, and e) improved design/expert systems methods for total aircraft coatings systems design (with AFRL/WPAFB). NDSU has continued to interact with other research groups performing advanced research on aircraft coatings, including the University of Missouri – Columbia (Prof. H.Yasuda), Univ. of Missouri-Kansas City (Prof. Jerry Jean), Boeing –Renton (Dr. J. Osborne), Rockwell Scientific (Dr. M. Kendig) and with Univ. Dayton Research Inst.(Dr. M. Khobaib) with Univ. Minnesota (Dr. E. Cussler) as well as AFRL –WPAFB (Dr. M.Donley), NAWC – Pautuxent Labs (Dr. Agarwalla), and ARL – Aberdeen Labs (Dr. J. Beatty and K.Chesonis). We have several proposals submitted to Federal funding agencies for extensions of these studies that are currently under consideration, and intend to continue to develop further parallel funding to expand and continue to pursue implementation of these important studies.