# REPORT DOCUMENTATION PAGE

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<td>Corrosion Protection of Al Alloys for Aircraft by Coatings with Advanced Properties and Enhanced Performance</td>
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<th>6. AUTHOR(S)</th>
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<tr>
<td>Gordon Bierwagen, Stuart Croll, Dennis Tallman, Qun Huo, Brian Allahar, Quan Su, Verena Bonitz, Dilhan Fernando, Duhua Wang</td>
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<td>AFSOR/NL</td>
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Final Project Report
Dec. 20, 2007
For Grant F9550-02-01-0368
To: U.S. Air Force Office of Scientific Research
Program Manager: Major Jennifer Gresham.

Corrosion Protection of Al Alloys for Aircraft by Coatings
with Advanced Properties and Enhanced Performance

From:
North Dakota State University
Fargo, ND 58105-5376

Principal Investigator:
Prof. Gordon Bierwagen
Department of Coatings & Polymeric Materials

Co-PI’s:
Dennis Tallman, Co-PI,
Stuart Croll, Co-PI,
Dean Webster, Co-PI (replaced Qun Huo who left NDSU)

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Abstract:
The report presents research that addresses research performed at NDSU for environmentally compliant corrosion protection in coatings systems of greatly extended lifetimes for present and future aircraft. For present coatings system, this work included modeling degradation in the bulk of a coating by the Monte Carlo methods developed in this laboratory for coating surface degradation, to test its applicability to the prediction of the lifetime of corrosion protection in coatings. Also work was performed to improve the analysis of the dielectric properties of organic coatings by the use of EIS, focusing on the higher frequency parts of the EIS spectrum dominated by these properties. This work supplements work already addressing these problems and adds new tasks and research activities to provide an enhanced effort. We also continued to support the scale-up and complete testing of the Mg-rich chrome-free coating system. This work was mainly performed in our AFRL contract through the CTIO, but advanced, new characterization studies and any major polymer modifications necessary to implement this system was performed under this study. Thus in this study, we extended the use of the SVET in the characterization and improved basic understanding of the manner in which Mg-rich primers provide damage protection. Extension of the cyclic temperature protocol developed earlier in this laboratory to the development of new polymers for aircraft coatings was performed to enhance the test protocol development work already underway as well as the inclusion of SVET techniques for characterizing the damage protective properties of multilayer coatings systems. We extended past sensor studies to examine them for the development of a Corrosion Health Monitoring array for entire aircraft. Application of combinatorial methods of materials science and high through-put screening to the development of corrosion protective aircraft coatings was continued by incorporating those portions as are feasible for this type of application from our test protocol as HTS methods for COMBI studies. New work on conducting polymers (CPs) for corrosion control coatings was performed to make them perform controlled-release of corrosion inhibitors used as CP dopants and initial studies of CP-based self-sensing corrosion control coatings. We also examined CPs for other react-and-control extensions of coatings performance properties that will make the coatings system of an aircraft take on more “smart skin” properties.

AFOSR Project Team: 2004-2007

Gordon Bierwagen
Principal Investigator
Advanced Characterization studies.

Dennis Talman
Co-PI
Conductive Polymer Development

Dean Webster
Co-PI
Polymeric Materials Synthesis

Stuart Croll
Co-PI
Assessment of Exterior Durability
Goal I. Prof. Gordon Bierwagen:
   A) New Developments for Mg-rich Coatings Technology
   B) Advanced Aircraft Coatings test Method Development, Sensor Studies and Test Data Analysis, including the use of Ionic Liquids in Coatings Characterization
   C) Development of Combinatorial-High Throughput Screening Methods for Corrosion Protective Coatings

Goal II. Prof. Stuart Croll:
   A) Coating Weathering Durability
   B) Spectroscopy on Model Polyurethane Topcoats
   C) Mechanical Properties of Model Polyurethane Topcoats
   D) Statistical Modeling of Coating Degradation

Goal III. Prof. Dennis E. Tallman:
   A) New Scanning Probe Studies of Novel Cr-free Active Coatings
   B) Examination of the Influence of Surface Preparation of Al alloy surfaces
   C) Mechanism of Action of Mg-rich Coatings
   D) Studies of Electroactive Polymer Coatings

Part 3. Results of Project
Work has been performed on a majority of the objectives listed above with the major accomplishments listed in Part 4 and a more detailed write-up included later in this report. One of the highlights of our activities is a full, rigorous characterization of the mechanism of protection of Al alloys by Mg-rich coatings. This was done under Goals I.A and III.C. This work verified earlier studies that implied the mode of corrosion protection by Mg-rich primers is by cathodic protection of Al alloy substrates and detailed this mechanism of protection. We also were able to successfully use ionic liquids in the EIS characterization of aircraft coatings, and with these liquids were able to measure the rate of water egress from coating films to supplement the measurements in aqueous electrolytes on water ingress. An emphasis on the use of modeling to interpret electrochemical data and spectroscopic from coatings in exposure was made during this work period. Various coatings have been investigated as possible Cr-replacements such as electroactive conducting polymers (ECPs), magnesium rich coatings which may act as a sacrificial coating for the aluminum alloy substrate. In the next work period, we will continue to emphasize Mg-rich Primer studies in support of more applied scale-up studies of these coatings.

Part 4. Accomplishments/New Findings

Goal I. Electrochemical Examinations of Aircraft Coatings + Considerations of Combinatorial/HTS Methods for Corrosion Control Coatings

A. These Mg-rich coatings are being scaled up at the 1-gallon level and have been submitted for outside testing to the Coatings Technology Integration Office (CTIO) at WPAFB as well as several companies interested in licensing the technology. We have complete scientific
verification by Open Circuit Potential (OCP) measurements and Potentiodynamic Scans that the protective action of these primers is indeed cathodic protection, and we have data to show that this protective action continues for over 9000 hours in a chrome free Mg-rich + topcoat system in ASTM 5894-96 (QUV + Prohesion) cyclic testing, far exceeding the 3000 hours of the standard Alodine chromated pretreatment + chromate pigmented primer + topcoat. The work on Self Assembled Monolayers for improved adhesion of corrosion protective coating systems to Al alloys is being included in our Mg-rich primers studies as Prof. Huo has left NDSU, but one of her students is staying and continuing work with Prof. Bierwagen in this area, and the work will be reported under this sub-goal.


C. Continued Development of HTS Methods for Development of Advance Aircraft Coatings A technique, SpeedEIS, is in the demonstration stage, and show promise to be a viable method for HTS of corrosion control coatings. We have added a capacity to perform sample temperature cycling to the equipment capabilities, and this should help screening of “good” samples.

Goal II. Weathering Durability Studies

The program at NDSU has tested statistical models, developed in prior years, for the deterioration in the surface properties of coatings with extensive data on pigmented films. The models not only represent the gloss and contact angle data well and appear to be physically reasonable, but they provide a basis that allows further deductions to be made about how performance varies by composition. The equations from the models follow the data and may provide robust, algebraic forms for extrapolating trends in weathering data to longer exposure times. Extrapolation is much more secure and conservative if based on scientific understanding. Quantitative understanding of degradation rates, as in these models, will permit quantitative comparison of degradation rates of coatings, or other materials, exposed in different environments or different series of exposures. Results suggest also that it may be possible to estimate the performance of pigmented formulations from results gained on un-pigmented polymers. Health monitoring using contact angle is proposed as a useful alternative to gloss measurements that may be easier to understand in terms of variations with composition and in the case of very loss gloss coatings. More detailed models for these surface properties are under development.

Work continues to understand how mechanical properties change during weathering exposure. These are important in uses that rely on the integrity of the coating. Not only is there an impact of chemical degradation, but molecular relaxation clearly plays a role depending on the polymer and the circumstances of the exposure. Molecular Dynamics investigations are under way to improve our basic understanding here. Solid state NMR has shown that chemical and physical effects can be seen in polyurethane materials.
Understanding how corrosion protective properties are maintained by coatings has produced some valuable insights. (See Goal I. B. Accomplishments, above) We have determined, from finite element modeling, that the shape of the water inclusion has a considerable impact on the EIS results. The use of the Brasher-Kingsbury model to calculate water content clearly only applies for water inclusions that are approximately spherical and will lead to considerable errors otherwise. The resistance-capacitance time constant may be indicative of inclusion shape and thus about mechanisms of corrosion protection. Other finite element calculations also suggest that surface roughness does not affect the slope of the Bode plots and that the search must continue to find the mechanism that causes the slope to diminish as a coating remains in exposure. Molecular Dynamics has progressed to the point that we are able to make predictions about the diffusion of water molecules through polyurethane polymers. The models that use dielectric calculations to predict changes in the equivalent circuit models used to interpret EIS results have been further refined.

**Goal III. Corrosion Control Properties of Novel Chromate free Active Coatings.**

A very common corrosion control strategy is to apply one or more layers of a coating to the metal to be protected. Such a coating may simply serve as a barrier between the metal and its environment, retarding the rate at which water, oxygen, and/or ions from the environment reach the metal surface. On the other hand, a coating may function as more than just a barrier. The coating may be an active coating in the sense that it contains or consists of a material than can interact chemically and/or electrochemically with the metal, altering its corrosion behavior. Conjugated polymers and Mg-rich coatings are example of active coatings currently being studied in our laboratory. We have used many methods this past year to extend our understanding and control of “active” corrosion protection by coatings, or as these types of coatings systems have been called by some (including Martin Kendig, Rudy Buchheit and S. Ray Taylor), “smart coatings.” We have used SVET, SLEIS SECM, Scanning pH Microscopy, Potentiodynamic Scans, general OCP, EIS and ENM methods to determine the mechanisms in which Mg-rich coatings and conductive polymer films (ICPs) protect damaged coatings. In conjunction with the activities of Goal I. A., we have developed several new methods and have acquired very interesting results to tell us of the importance of basic and local measurements in understanding the performance of the next generation of corrosion protective coatings.

6. **Publications**

*Journal Article Publications: 34*


32. S. Croll, S. Liu, B. Hinderliter, “Predicting Changes in Coating Properties During Weathering,” Tri-Services Corrosion Conference, Orlando FL, Nov 14 – 18th, 2005


b. Consultative and Advisory Functions

G.P. Bierwagen
- Editor –in-Chief *Progress in Organic Coatings*
- Scientific Planning Committee, Coatings Science International Annual Meeting, Noordwijk, the Netherlands, June 2005

D. E. Tallman:

Stuart Croll:
- Editorial board of “Journal for Coatings Technology”
- Editorial Board of “Progress in Organic Coatings”
- NDSU College of Science and Mathematics member of Curriculum Committee.
- NDSU Laboratory and Chemical Safety Committee, Chair.
- NDSU Academic Affairs Committee, member

c. Transitions

3 PhD’s to: Verena Bonitz(Bierwagen), Allan Skaja (Croll) Duhua Wang (Bierwagen) were awarded as a consequence of this grant.

8. New Discoveries, inventions, or Patent Disclosures
   Patent Application RFT-140, No Serial number assigned as of this date
   Filed 09/15/06
   Title: Coatings and Coating Systems (Chromate Free Corrosion Protection)
   Inventors: Gordon Bierwagen, Dante Battocchi and Duhua Wang