**REPORT DOCUMENTATION PAGE**

**Title:** Characterization, Modeling, and Accelerating Emulation of Aircraft Coating Exposure and Degradation.

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**Abstract:**
The Air Force stations its aircraft in many geographical locations worldwide, and some of these sites have specific exposure conditions and atmospheric chemistry that make them especially "potent" in their effects on aircraft coatings. In a period in which the Air Force is making the transition away from chromate-based corrosion protection for its air fleet, it is very important that the test methods used in qualifying new protective coatings and metal pretreatments properly reflect the stresses and conditions to which the aircraft are exposed. Further, these tests must be truly accelerated tests in that they MUST accurately reflect the stresses and hazards that the aircraft and its coatings systems will see during its lifetime. The present suite of tests now used in coating accelerated testing need to be upgraded to reflect the current state-of-the-art in environmental science concerning the exposure which the aircraft will really see, as well as the state-of-the-art in measurements and modeling of coating degradation and failure in the field and the laboratory. NDSU proposes to do an extensive review and update of the suite of tests now currently used to qualify coatings and coating systems for DoD aircraft. It will choose those tests, such as ASTM B117, that have obvious flaws, and develop or implement alternate test protocols that reflect the best current science and document these measurement as appropriate test methods, including the accelerating factors of the test, and the modeling of the test to make it predictive of future performance of the coatings. The coatings used in developing the improved methodologies will include both the existing chromate-based systems upon which all of the present tests and qualification procedures have been built (and biased as well), as well as all the best of the chromate replacement coatings such as the Mg-rich technology from NDSU.
### INSTRUCTIONS FOR COMPLETING SF 298

15. **SUBJECT TERMS**
- NDSU, modeling, geographical, pretreatments, coatings, environmental, and Mg

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19b. **TELEPHONE NUMBER** (include area code)
Final Report to Air Force Office of Scientific Research

September 30, 2009

Re: Grant #: FA9550-07-1-0370

Program Manager: Major Michelle Ewy

Characterization, Modeling, and Accelerating Emulation of Aircraft Coating Exposure and Degradation.

Prepared by

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NDSU Dept. 2760
PO Box 6050
Fargo, ND 58108-6050

Prof. Gordon P. Bierwagen

Principal Investigator

Prof. Stuart Croll & Prof. Dennis Tallman,

Co-PI’s
Project Team

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<td>Gordon Bierwagen</td>
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<td>Dante Battocchi</td>
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Abstract of Work Effort from Project Proposal:

The Air Force stations its aircraft in many geographical locations worldwide, and some of these sites have specific exposure conditions and atmospheric chemistry that make them especially “potent” in their effects on aircraft coatings. In a period in which the Air Force is making the transition away from chromate-based corrosion protection for its air fleet, it is very important that the test methods used in qualifying new protective coatings and metal pretreatments properly reflect the stresses and conditions to which the aircraft are exposed. Further, these tests must be truly accelerated tests in that they MUST accurately reflect the stresses and hazards that the aircraft and its coatings systems will see during its lifetime. The present suite of tests now used in coating accelerated testing need to be upgraded to reflect the current state-of-the-art in environmental science concerning the exposure which the aircraft will really see, as well as the state-of-the-art in measurements and modeling of coating degradation and failure in the field and the laboratory. NDSU proposes to do an extensive review and update of the suite of tests now currently used to qualify coatings and coating systems for DoD aircraft. It will choose those tests, such as ASTM B117, that have obvious flaws, and develop or implement alternate test protocols that reflect the best current science and document these measurement as appropriate test methods, including the accelerating factors of the test, and the modeling of the test to make it predictive of future performance of the coatings. The coatings used in developing the improved methodologies will include both the existing chromate-based systems upon which all of the present tests and qualification procedures have been built (and biased as well), as well as all the best of the chromate replacement coatings such as the Mg-rich technology from NDSU, the Deft/UMR materials and others as they are available. It will then attempt to recommend, based on its own work and the work of others the best suite of measurements and models for coating performance that exist or can be easily developed for the AF.

Below is an outline of this research program as taken from the original project proposal.
Program Outline

Characterization, Modeling, and Accelerating Emulation of Aircraft Coating Exposure and Degradation

1. **Assessment of Exposure in Aircraft Coatings**
   - 1.1 Environmental Factors
   - 1.2 Specific Studies on the Environmental Effects of Exposure to Moisture
   - 1.3 Advanced Assessment of the Transport of Water in Organic Coatings
   - 1.4 Characterization of the Performance of Mg-rich Primers in Exposure

2. **Modeling of Exposure**
   - 2.1 Modeling of Exposure and its Effect on Coatings
   - 2.2 Modeling of Water Transport in Organic Coatings
   - 2.3 Modeling of Active Pigmented Coatings

3. **Development of Test Methods**
   - 3.1 Mechanical strains, Voids, Cracks and Fatigue
   - 3.2 Combinatorial Approaches to Coating Degradation
   - 3.3 Consideration of New Corrosion Protection Test Method
   - 3.4 Accelerated Testing by Enhanced Transport Processes

4. **Initiating research topic**
   - Ionic Liquids as Electrochemical Solvents for Coatings Characterization and Coatings Deposition on Metal Substrates

In addition to the work above, we included studies of Flexible Mg-rich Primers for Aircraft at the request of Mike Spicer of the AFRL/WPAFB Coating Technology Integration Office. This work is mainly contained in the MS Thesis of T. Chen, and was presented publicly on October 14, 2010 at the NACE Eastern Area Conference in Alexandria, VA.

The work presented in detail in this report is that work as yet unpublished that was performed under this grant. We will cite references to published work when there is no original unpublished work to be given. We identify below the published work from full or partial support by this Grant. Graduate student theses describing student research that was supported in full or in part will be cited as pertinent.
We also append the two annual reports on the contract as pertinent to summarizing the project effort and results of the research effort performed under this grant.

**ANNUAL REPORT 1: Reporting Period: September 1, 2007 to July 31, 2008**

**Program Manager: Major Jennifer Gresham**

The objectives of this program remain unchanged from the original statement of work.

Annual accomplishments:

**GP Bierwagen Group:** Work was performed on the use of ionic liquids in emulating cyclic wt-dry exposure using ionic liquids. The acceleration of coating failure using low velocity laminar flow of electrolyte indicates an increase in failure rate without changing the mechanism of failure can be achieved. We have been expanding our studies of the AC-DC-AC test protocol for acceleration of coating failure in aircraft coating systems, and we used electrochemical noise methods/shot noise to determine the mechanism of corrosion failure under the accelerating conditions.

**Stuart Croll Group:** Finite difference calculations have been made of the diffusion of water into coatings in different weathering cycles. They demonstrate very clearly how accelerated testing protocols may concentrate water at different depths than may natural weathering. Thus coating failure due to adhesion loss or hydrolysis can be very different between accelerated testing protocols, depending on temperature level and cycle period, and will be different, in general, to failures experienced in the field. This provides clear insight into discrepancies between accelerated weathering tests in the laboratory and in field experience.

**Dennis E. Tallman Group:** This project deals with the thermal cycling and the wet/dry cycling of organic coatings employing ionic liquid media, research that was led by Research Assistant Professors Kerry Allahar and Brian Hinderliter. Some of the results are discussed above. The results of these studies are also discussed in detail in the publications cited below. Additionally, we have continued our studies of electron transfer at AA 2024-T3 using scanning electrochemical microscopy. We have characterized the types of intermetallic particles that dominate the electron transfer process and have found correlations with the surface conductivity of these particles as measured by conducting atomic force microscopy. We have written a LabView based program that interactively fits theory to experimentally measured probe approach curves, permitting a quantitative assessment of the apparent electron transfer rate constant and how it varies over the heterogeneous surface of AA 2024-T3. These results are important for understanding electrochemical interactions between active coatings (such as conjugated polymer and Mg-rich coatings) and the aluminum alloy. Details are available in the publications cited below.

**Archival publications (published) during reporting period by**

**Bierwagen Group:**


B. Hinderliter, K. Allahar, G. Bierwagen, D. Tallman and S. Croll, “Using ionic liquids to measure coating properties via electrochemical impedance spectroscopy (EIS),” accepted, Journal of Coatings Technology & Research

Tallman Group:


**Participation at Meetings/Presentations 2008-2009:**

The personnel on this project have attended many meetings related to coatings and electrochemistry over this past year, and it is hard to separate specific meetings and presentations that were attended only for this program. However, most of the senior professional staff on this program attended the DoD sponsored Tri-Service Corrosion Conference in Denver, CO in December 2007, and made presentations at this meeting. **As a matter of fact, NDSU had the largest number of presentations at this meeting of any of the academic institutions receiving DOD support.** A list of the presentations that can be specifically tied to this project are given below:

Presentations:


ANNUAL REPORT 2: Reporting Period: September 1, 2008 to August 31, 2009

Change in AFOSR program manager: **Major Michelle Ewy has replaced Maj. Jennifer Gresham as our AFOSR Program Manager**

The objectives of this program remain unchanged from the original statement of work.

**Annual accomplishments:**

**GPBierwagen Group:** Work was continued on the use of ionic liquids in emulating cyclic wt-dry exposure using ionic liquids. The acceleration of coating failure using low velocity laminar flow of electrolyte indicates an increase in failure rate without changing the mechanism of failure can be achieved. We are now using embedded electrodes of the type developed in our lab in conjunction with flowing electrolyte to gain further insight to the mechanisms of this type of accelerated failure. The characterization of the cathodic protection of Mg-rich primer for aluminum substrates was continued. The transmission line model was applied to electrochemical impedance spectroscopic data associated with the degradation of a Mg-rich primer. The application of embedded sensors for real time monitoring of Mg-rich primers was performed with the data and analysis reported. The investigation of the AC-DC-AC test protocol for acceleration of coating failure in aircraft coating systems was continued with efforts utilizing embedded sensors demonstrating the applicability of this test method coupled with embedded sensors. New characterization techniques based on Low Angle Microtomy for sample preparation were developed and used in examining exposed samples to determine effects of accelerated aging. Work has been performed on the development of an embeddable reference electrode for use in metal rich coatings to provide continuous monitoring of the OCP of such a system to continuously measure cathodic protection of metal substrates and the change in such coatings on accelerated exposure.

**Stuart Croll Group:**

Values for the physical properties of coatings are necessary for both the predictive modeling and understanding the connection between accelerated modeling and natural weather exposure. Appearance properties are often dominated by processes occurring at the outer surface and protective properties depend also on the bulk properties. We have found that the natural time dependence of polymer response to any stress lasts longer than the cycle period used in accelerated weathering. Thus mechanical stress does not relax much and builds more in accelerated testing than it does in the diurnal (and longer) cycles of natural conditions. Thus in order to correlate the results of accelerated weathering, we need to factor in higher and different levels of bulk stress and mechanical properties compared to those that would be characteristic of natural weathering.

Photodegradation or mechanical scratches produce surface features in polymers that may relax and diminish after they have been produced. In order to predict, if possible, the connection between accelerated weathering and natural exposure, this relaxation was studied in order to quantify better the damage accumulating in a typical cycle in either environment. Photodegradation-induced roughness and mechanical indentation, near the surface (outer 200 nm) exhibit a significantly lower glass transition
temperature, $T_g$, than a bulk measurement of $T_g$. This appears to be genuine and not an artifact of experimental technique or adventitious chemistry. This phenomenon is well known in thermoplastic polymers and now makes the performance of crosslinked coatings more complicated. The practical outcome of this is that the effect of exposure temperature on physical property responses cannot be understood using standard, bulk measurements of glass transition temperature. In addition, when water is absorbed into the coating it softens the polymer again, so water transport and location (as reported last year) makes further differences. Relating laboratory accelerated tests to natural weathering requires that we understand the conditions and effects in both, at a very detailed level.

**Dennis E. Tallman Group:**

Studies by D. Tallman emphasized the elucidation the role of oxygen in protective coatings performance during their active lifetime of protection. The role of oxygen in the galvanic coupling of poly(pyrrole) and AA 2024-T3 has been fully elucidated and is now published (Yan, Tallman and Bierwagen, 2008).

Studies of electron transfer at AA 2024-T3 using SECM have continued. Using the LabView™ program developed during the previous project period, we have now fit experimentally measured probe approach curves to theory, permitting a quantitative assessment of the apparent electron transfer rate constant and how it varies over the heterogeneous surface of AA 2024-T3 (Jensen et al., manuscript in preparation). These results are important for understanding electrochemical interactions between active coatings (such as conjugated polymer and Mg-rich coatings) and the aluminum alloy. Work was initiated using SECM in combination with scanning electron microscopy and energy dispersive x-ray analysis to study nucleation sites for conjugated polymer electrodeposition on AA 2024-T3. In particular, the role of secondary phase heterogeneities in the nucleation and growth of polymer is being investigated.

Archival publications (studies with at least partial support by this Grant) during reporting period by

**Bierwagen Group:**


**Tallman Group:**


Croll Group: (see above for publications jointly with other Groups on this project)


Participation at Meetings/Presentations:

The personnel on this project have attended many meetings related to coatings and electrochemistry over this past year, and it is hard to separate specific meetings and presentations that were attended only for this program. However, many of the senior professional staff on this program attended the DoD Corrosion Conference in Washington DC in August 2009, and made presentations at this meeting. A list of the presentations that can be specifically tied to this project are given below:

Presentations: (First person in author list or underlined author were presenters)

5. Xiaodong Shi, Brian R. Hinderliter, Stuart G. Croll, “The effect of moisture transport on corrosion protective coatings, or, being careful with accelerated weathering,” Army Corrosion Summit, Clearwater, FL, Feb 3-5, 2009
9. Kerry Allahar, Duhua Wang, Dante Battocchi, Gordon Bierwagen, “Electrochemically detecting defects in an Air Force topcoat/Mg-rich primer system with embedded electrodes.” Research in Progress Session 1, NACE Corrosion/2009, Atlanta, GA.
18. Dennis E. Tallman, Maocheng Yan, Seth C. Rasmussen and Gordon P. Bierwagen, “Neutral and n-Doped Conjugated Polymers for Corrosion Control of Aluminum Alloys,” Fourth International Conference on Advanced Materials and Nanotechnology (AMN-4), February 8-12, 2009, the University of Otago, Dunedin, New Zealand, Invited Speaker.
For the work period Sept. 2009 to June 30, 2010, the termination of the contract, the following archival publications resulted, all or in part, from this grant:

**Bierwagen Group**

K. Allahar; Dante Battocchi, Gordon P Bierwagen, Dennis E Tallman, “Thermal degradation of a Mg-Rich primer on AA 2024-T3,” submitted to *Corrosion Science* March 2010


Quan Su, Kerry N. Allahar, Gordon P. Bierwagen, “In-situ embedded sensor monitoring of an Air Force primer beneath a topcoat exposed to atmospheric humidity and thermal conditions,” *CORROSION, 66* (2010) 066001


The following Presentations of results generated, all or in part, from this grant in the time frame Sept 2009 to June 30, 2010, are as follows:


Gordon Bierwagen, “Mg-Rich Chromate Free Primers for Aircraft,” Plenary Lecturer for PaintIstanbul Congress., Turkish Paint Industry Association (BOSAD) presented September 23-26, 2010

Gordon P. Bierwagen, a* Kerry N. Allahar a, Vinod Upadhyay a “Extracting New Information from Enhanced AC-DC-AC Accelerated Testing of Coated Metals,” EIS 2010 June 6 - 11, 2010 • Hotel Tivoli Carvoeiro • Carvoeiro, Algarve, Portugal


A Program Review Meeting in Alexandria VA for the AFOSR 2009 Surface and Interfacial Science Portfolio took place Oct. 13, 2009. For this grant the following information was presented:
AFOSR Program Review
for Grant FA9550-07-1-0370:
Characterization, Modeling, and
Accelerating Emulation of Aircraft
Coating Exposure and Degradation

Prof. Gordon Bierwagen, PI
Dept. of Coatings & Polymeric Materials
North Dakota State University

AFOSR Review 13 Jan 2009

Outline of Presentation

I. Brief Discussion of Work Through 2009
II. Work of NDSU Group in 2009
   A. Room Temperature Ionic Liquid Studies
   B. CPVC Studies
   C. Characterization Studies
      1. Low Angle Microtome Methods
      2. Fluorescence Microscopy
   D. Flow Induced Degradation Studies
III. General Issues on Accelerated Testing and
     Lifetime Prediction of Aircraft Coatings
Research Activities for AFOSR

Current
- Mg rich primer
  - Experiments conducted with temperature as a variable to determine consistency of modeling parameters with Arrhenius behavior
- Monitoring Mg-rich primer/topcoat with embedded sensors
  - Experiments conducted with scribed panel to determine the influence of defects on the EIS and ENM parameters
- Modeling of scaled OCP relaxation associated with Air Force coatings
  - Experiments conducted with temperature as a variable to determine consistency of the modeling parameters with Arrhenius behavior
- Dynamic Bend testing of Air Force coatings under accelerated conditions
- Influence of atmospheric conditions and UV light exposure on the degradation of corrosion barrier protection of Air Force coatings

Diffusion Coefficient derived from Fitting of EIS at $10^4$ Hz

3 replicates at each temperature are consistent
- Diffusion coefficient with water ingress is higher than water egress (RTIL as electrolyte)
- Room temperature diffusion coefficients return to initial values
What have we learned thus far in Coatings with new RTIL’s

- RTIL’s allow characterization of coatings in drying unavailable in aqueous electrolytes
- Continuous system monitoring at single frequency (greater than system response time) in EIS gives dynamic picture of processes occurring in coating exposure and field use
- Data from System now available:
  - Local Conductivity, Capacitance of Coating during drying as well as drying cycles, Volume fraction of water vs time in coatings, insight into effects of conductive pathways in coatings, Diffusion coefficients for water in wetting as well as drying
- In conjunction with measurement techniques, they offer new insight into dielectric effects in coatings, especially transport effects

Thermal influence on ac-dc-ac accelerated testing

- ac-dc-ac cycles
  - a.c. step: EIS (ENM)
  - cathodic potential d.c. step
  - rest period: relaxation of OCP

- Barrier property was consistent with Arrhenius behavior

- Modeled scaled E_in, relaxation profile with 3 characteristic time model
  - Characteristic times
    - diffusion (10^4 s) > dielectric relaxation (10^3 s) > charge transfer (10^2 s)
  - Pre-exponential parameters consistent with Arrhenius behavior in 35 °C to 55 °C range
Influence of mechanical strain on Mg-rich primer performance

- Similarity between flat and strained panels during CP loss
  - Barrier property
  - Dielectric property at 10 kHz
- 6% strain yielded 27% loss in CP

- Transmission line model fit data
  - Similarity between flat and strained parameters as functions of $E_{\text{oc}}$
  - Parameter $R_3$ had a faster change with time indicating that the faster loss of CP was due to the interfacial processes
  - Strain caused defects by Mg particles thereby increasing surface area

Dynamic Exposure Chamber Samples and Side View
Thermal influence on Mg-rich primers

- Transient profiles for $E_{OC}$
  - Distinguishable stages
  - Similar for different temperatures
- Cathodic protection (CP) loss
  - Faster at higher temperatures
  - Increases in $Z_{0.01\text{Hz}}$ and $C_{10\text{kHz}}$
- Transmission line modeling
  - Fit for range 0.01 Hz to 1 kHz
  - Loss in CP associated with changes in interfacial resistance parameter
- Arrhenius plot of parameters
  - Opposite signs for $R_a$ and $R_l$ supports model
  - Increase in $E_A$ for conductivity with loss in CP supports model

Pigment Volume Fraction and Particle Packing Effects in Coating Design and Performance

- Modeling "Coarseness" of pigment-polymer distribution + allowing voids gives realistic predictions of film behavior.
- Calculations & model yield qualitative agreement with real systems.
- Hard Sphere/Monte Carlo Packing Modeling gives extraordinary insight into particle packing in coatings films.
- Work ongoing to include percolation analyses into coating modeling.
- We are continuing studies of packing efficiencies in our work (discussed below) on metal-rich primer coatings. We are examining shape and orientation effects in particle packing as well as connectivity of particles in corrosion protection.
- Future work will model particle packing, flocculation, etc. and test results quantitatively with experimental film properties.
- Further work needs to be done to account for particle size distribution effects.
SEM Micrograph of Ecka 3820 Mg Pigment in an Epoxy Resin After 15 Days of Prohesion Exposure

EDX Elemental Analysis for Coating with 15 Days of Prohesion Exposure

Magnesium  Original Micrograph  Oxygen
Microscopy (Contd.)

SEM Cross section

Confocal Raman microscopy mapping

3820 Mg-rich Primer, PVC = 42\%
in Prohesion Chamber for 1685 hr.

A: carbonate + sulfate

B: Polymer matrix: epoxy

C: Mg particles
SVET – Directly show cathodic protection

LNR90 44%, 0 hr. in DHS

Studies of Electron Transfer at Aluminum Alloy Surfaces by Scanning Electrochemical Microscopy

Daewoo S. Thomsen, North Dakota State University

ACCOMPLISHMENTS
- Demonstrated that fastest electron transfer occurs at IMPs, but rate depends on composition of the IMP.
- Demonstrated electron transfer on the alloy matrix under acidic conditions.
- Obtained estimates of electron transfer rate constants.

DOD PAYOFF
- Better understanding of Al alloy corrosion.
- Insight into the design of improved active coatings for corrosion control.

FUTURE WORK
- Assess influence of alloy surface preparation on electron transfer rates.
- Reduce size of SECM probe to obtain more reliable data on small IMPs.
New Recent Issues

- Work of Prof. Tallman’s group implies O\textsubscript{2} Sequestration/Scavenging by active materials, including Mg particles in Mg-rich primers, may explain some of the corrosion protective function of active coatings.
- In the case of the Mg-rich systems, the O\textsubscript{2} Scavenging effects may possibly be interpreted by Cussler’s analysis of chemically active species in a film.
- The lag time $\tau$ for a diffusing material such as O\textsubscript{2} without scavenging is $\tau = t^2/6D$, where $t$ is the film thickness and $D$ is the diffusion coefficient. When there is scavenging of the diffusing material, in our case O\textsubscript{2}, the lag time is $\tau = t^2/6D(1 + 3C_{\text{scav}}/vHC_{O2})$ where $v$ is the stoichiometric coefficient for the scavenging of O\textsubscript{2}.

Recent Issues

- We are beginning studies to examine the effects of this scavenging on the later stages of Mg-rich coating lifetime. Current results indicate corrosion protection by the MgR systems even when there is no longer cathodic protection. This scavenging effect may contribute to the extra-ordinary (MgR primer + topcoat) that has been observed within the AF and other military services.
Particle Size Distribution

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<th>Particle Size Distribution of Mg-rich Pigment</th>
<th>Particle Size Distribution of Perovskite (110) Pigment</th>
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<td>Particle Size Distribution of Perovskite (110) Pigment</td>
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SEM Images of Mg-rich coating
Experimental Setup

- AA 2024-T3 substrate
- Mg-rich primer
  - 5 minute epoxy for ERE
- Polyurethane topcoat

Objectives

A. Fabricate and embed Ag/AgCl reference electrodes
   - Adhere wire electrode between primer and topcoat
   - Lead to external equipment must be secure
B. Obtain OCP measurements using the ERE
   - Constant immersion testing
   - Apply potential and monitor response
C. Investigate in-situ performance via B117 salt spray
   - CCP and Electrochemical Impedance spectroscopy (EIS)

Silver (Ag) wires
50 μm diameter
Chemically oxidized
0.03M FeCl₃
60 seconds
AgCl layer deposits
Stable Ag/AgCl mixed potential is established
Experimental Methods – I. OCP

• Multiplexed potentiostat
  – OCP vs. ERE, OCP vs. saturated calomel electrode (SCE)
  – Near-simultaneous measurements
• ΔE should not change over time
• E vs. ERE expected to be -300 mV to -900 mV

Results – I. OCP

• E vs. ERE is approximately -600 mV
  – Ranges from 25 to 175 mV more positive than $E_{SCE}$
Results – II. Potentiodynamic

- EREs respond favorably
  - Quickly
  - Stable

- OCP slope is near imposed rate

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<td>Imposed</td>
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<td>4.0</td>
<td>4.6</td>
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II. Fracture Strength
Crucial to many properties, inc. corrosion

Griffith’s criterion for stress at fracture (toughness) in brittle materials:

\[ \text{Stress}_{\text{init}} = \sqrt{\frac{2EG}{\pi T}} = \text{Stress}_{\text{internal}} + \text{Stress}_{\text{external}} \]

Assuming the largest initiating crack (pit) is \( n \) standard deviations deep (using zero order kinetics):

\[ \text{Stress}_{\text{init}} = \sqrt{\frac{2EG}{2n\sigma_{\text{max}}^2 + kt}} \]

Simplifying and scaling to initial fracture stress gives:

\[ \frac{\text{Stress}_{\text{inc}}(t)}{\text{Stress}_{\text{inc}}(t=0)} = \left(1 + \frac{kt}{\sigma_{\text{init}}^2}\right)^{-1/2} \]

- Possible linkage between gloss and toughness via \( k \) and \( \sigma_{\text{init}} \)
Application to Fracture Strength


The line is a fit (zero order) obtained from raising the relative fracture strength to 4th power. Plausible fit, but too few data to be conclusive.

If there were more data points, we could have justified some of the options below.

Corrosion Protection

Model of Electrochemical Impedance Spectroscopy

- If water gets in via Diffusion ($t^{1/2}$) and linear $t$, damage process (Case II Diffusion):
  - Then the resistance (low frequency impedances) of the coating will diminish as the water reaches out that depth (data from Gordon Bannagan).
- Thickness of the film, $d$, is reduced by: $d(t) = d_0 - (D_2t^2 + D_3t)$
- We can calculate the impedance of the film, assuming a parallel RC equivalent.
- Coating life is limited at rundown
- Failure is when water arrives at substrate
  - vs. size of thin spot, plugging

- N.B. Percolating water channels seem to follow a log-normal arrival time distribution (Monte Carlo calculation)
- $D_i$'s to left will be sealed by the exposure cycle period
Total Water Uptake in Cyclic Exposures

- The total water mass in the coating increases at the end of each wet cycle.
- The dry cycle removes some water, but not all.
- Depends on time and temperature.
- The cycles are not yet equivalent here.

Possible water transport with cycling

Schematic illustration of water molecule distributions. Differences may occur depending on whether there is time for the whole coating to saturate or dry.

- Depending on where the water is, and whether the material $T_0$ is affected:
  - the rate of degradation chemistry may be altered
  - the rate of any physical change may be altered
  - failure mechanism may be different, e.g., adhesive vs. cohesive
Time – Dependence example: Stress relaxation in cycles

- Equivalent length of experimental time at both temperatures;
- Stress built up in the short cycles; much less in long cycles
  - Short cycles may cause failures but long cycles may never
- How about moisture?