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LATERAL DIFFUSION IN COATING SYSTEMS
Lateral Diffusion in Coating Systems

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2009 U.S. Army Corrosion Summit, 3-5 Feb, Clearwater Beach, FL
REASON FOR RESEARCH

- “The total direct cost of corrosion was determined to be $279 billion per year, which is 3.2 percent of the U.S. gross domestic product (GDP). Indirect costs to the user (society costs) are conservatively estimated to be equal to the direct costs.”¹

- Pollution
  - Removed paint then repaint
    - Volatile organic compounds
    - Constituents of original paint (lead ...)
  - Paint and corrosion products dissolved into environment
    - Chromates, organics, metal (alloying components)

- Safety

IS DIFFUSION IMPORTANT TO CORROSION?

- Corrosion is an electrochemical reaction of metals with the liquid environment

- Why do we care about diffusion?
  + Corrosion requires electrical contact, electrolyte
  + Corrosive ion transport, Cl^-
  + Corrosion inhibitors (chromates)
  + Optimize drying cycles
  + Design better accelerated testing protocols

- Whatdiffuses?
  + Oxygen, water, chromates and other soluble inhibitors
  + Residual solvent or hydrolysis products out
  + UV absorbers, free radicals, pollutants
DIFFUSION IS IMPORTANT FOR:

- Water and ion movement
  - Through coating
  - Around pigments, fillers and ion exchange
- Movement of corrosion inhibitors
- Across substrate-coating interface
- Through oxide layers
COATING AS A BARRIER

• Barriers, such as coatings, slow transport of water to substrate
  • Delay onset of corrosion
  • Bottleneck for corrosion progression
• Pigments and fillers make the diffusion path longer
• Ion exchange can remove environmental hazard en route
• Water acts as a conveyer for ions


Figure 1. Sealing the underlying metal from contact with its corrosive environment, the barrier effect stops oxygen and water from penetrating down to the steel to create corrosion.
LATERAL DIFFUSION

- Water advance water along the substrate
- The advance of the water front includes a loss term as the water diffuses up through the topcoat
IMPACT OF LATERAL WATER DIFFUSION

- Hydrolysis of adhesion bonds
- Reaction with residual contaminants (Cl)
  - Osmotic pressure – blister formation
  - Corrosion catalyst
- Transport of active corrosion protectors
When corrosion begins, diffusion occurs in the plane of the coating. Diffusion is required to balance charge. Often salt required to defeat metal oxide layer. (LeChartlier principle)

Corrosion needs:
- Continuity between anode and cathode
- Focus on water movement

ASPECTS OF COATING SYSTEM THAT PROTECT

- Surface topography
  + Sanding
- Surface cleanliness
  + Chlorides and sulfides
  + Oils (protect metal, reduce adhesion)
- Pretreatment
- Primer
- Topcoat
TESTING METHODS FOR CORROSION PROTECTION

- Gloss
- Color
- Contact angle
- Visual indication of blister formation

- Difficult to test pretreatment or surface treatment separately
  - Tracers
  - Indicators
  - EIS (traditional setup tests directly below cell)
ORGANIC BARRIER COATINGS

Organic coating

H₂O

O₂

Metallic substrate

Prohesion test

Wet step

Dry step
CYCLIC DIFFUSION

- Surface is exposed to water, then dry air
- Real-life and accelerated weathering
  - ASTM D5859
    - 1 week of:
      - 4 hours UV exposure at 60°C
      - 4 hours of condensation at 50°C
    - 1 week of:
      - 1 hour salt spray at 25°C
      - 1 hour dry at 35°C
PHOTOCHEMICAL DEGRADATION (WATER AT SUBSTRATE)

- Average wet exposure duration
- Overall fraction of time exposed to water
EXPERIMENTAL SETUP

- Scraped paint filled with solution
- Counter Electrodes: 1, 2, 3, 4, 5
- Working electrode connection
- Water diffusion
TEST

- Army Primer
- Army Topcoat
- Harrison solution
- Conducting Gels
- EIS spectra
Initially impedance at high and low frequency have high impedance.

High and low frequency Impedance drop as water reaches
IMPEDEANCE TO SECOND CELL

Zmed (Ohms) vs Frequency (Hz)

- 0 Hours
- 1.3 Hours
- 3.7 Hours
- 20.6 Hours
- 44.6 Hours
- 68.8 Hours
- 94.2 Hours
- 120.8 Hours
- 146.4 Hours
- 163.8 Hours
- 188.6 Hours
- 214.8 Hours
- 238.6 Hours
- 263.5 Hours
- 332.6 Hours
- 412.7 Hours
- 525 Hours
- 741 Hours
Impedance to 3rd Cell

BK 1-3

Zmod (Ohms) vs. Frequency (Hz)

Time points: 0 Hours, 1.3 Hours, 2.5 Hours, 19.6 Hours, 43.3 Hours, 67.5 Hours, 93.4 Hours, 119.4 Hours, 145.0 Hours, 162.4 Hours, 187.3 Hours, 213.4 Hours, 237.5 Hours, 263.3 Hours, 332.2 Hours, 411.3 Hours, 524.3 Hours, 740 Hours
SUMMARY

- Lateral diffusion is being investigated to rank:
  + Surface preparations
  + Surface cleaning technologies
  + Pretreatments

- Testing is designed to test complete systems
IMPACT OF LATERAL DIFFUSION

- Corrosion advance
  - Time to connect cathodic and anodic regions
- Concentration of the water needs to be sufficient for ion transport
  - Understand metal surface treatment, surface preparation, primer, topcoat (image thermal)
INTRODUCTION

- Accelerated weathering protocol
  + Need to test system designed to last for decades
- Reciprocity shown based on dose (Chin et. al. 2005)
  + But accelerated weathering protocols don’t always match environmental exposures
- Simulations allow:
  + Physical processes can be combined (UV absorption and diffusion)
  + Results to be quickly analyzed unambiguously
  + Experimental systems hard to design
COMPUTATIONAL TOOLS AND SELECT APPLICATIONS

- Finite element analysis
  - Electromagnetic response (EIS and Dielectric spectroscopy)
  - Diffusion
  - Multiphysics (couple the above)

- Monte Carlo – Coating as a composite breakdown

- Finite difference – coupled photodegradation/ hydrolysis

- Molecular dynamics – simulate ion and water transport

- Quantum chemistry – polymer chain scission location
WHY DEVELOP MODELS OF COATING SYSTEMS?

- Physically based equations/models allow:
  - Extrapolation (Lifetime prediction)
  - Understanding of processes impacting measurement (Occam’s razor) – **enhanced/optimized design**
  - Troubleshooting and new technology evaluation
  - Compare various accelerated weathering standards with various service environments
    - Predicting service life and property changes with time
    - Develop more realistic/representative accelerated tests
    - Gain insights into degradation mechanisms

*Modeling allows testing hypothesis that are difficult or impossible to do experimentally.*
- Take pigment particle size and number
- Divide coating binder into average coverage