Functionalized Nanoparticles and Nanostructures as Carriers for Organic Corrosion Inhibitors

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Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

Corrosion Protection by Coatings

- **Passive Protection**
  - Barrier to electrolyte permeation
    - Requires good adhesion, flexibility, toughness
- **Active Protection**
  - Relies on inhibitors when barrier properties breached
- **Inhibitor needs**
  - Water solubility (but not too much)
  - Hydrophobicity (to displace water from metal surface
  - Reactivity with metal or high adsorption strength
  - Delivery mechanism

Challenges for Chromate Replacements

- **Inorganic non-chromate replacements are less effective and more soluble than chromates**
  - Higher concentrations lead to flushing and osmotic blistering
- **Chromates are mixed (e.g. anodic and cathodic) inhibitors**
  - Non-chromates are generally cathodic inhibitors
- **For organic corrosion inhibitors low specific gravity is a problem**
- **Reactivity of functional groups of organics with resins can affect resin cure and trap inhibitors**

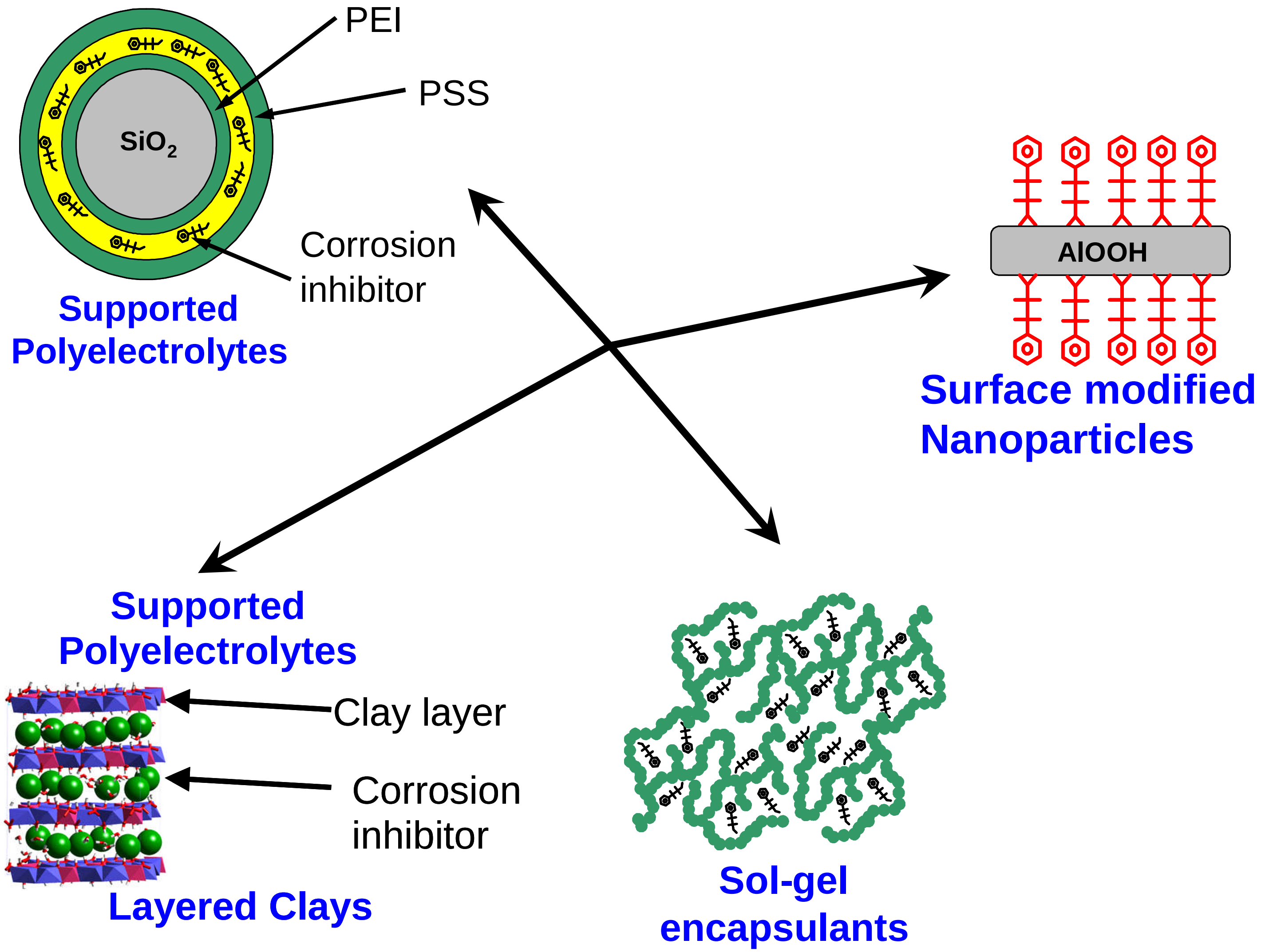
Organic Corrosion Inhibitors

- Organic molecules offer the best chance for discovery of novel, effective and low toxicity corrosion inhibitors
- The combination of only four elements C, N, O, and S, limited to a maximum of 30 non-hydrogen atoms could produce 10^{60} unique molecules.
  - Only 2.6×10^{7} organic and inorganic compounds have been synthesized since the foundation of organic chemistry in the 19th century.
- Quantitative Structure-Activity Relationships for organic corrosion inhibitors are being developed to guide corrosion inhibitor design

Corrosion Inhibitor Delivery

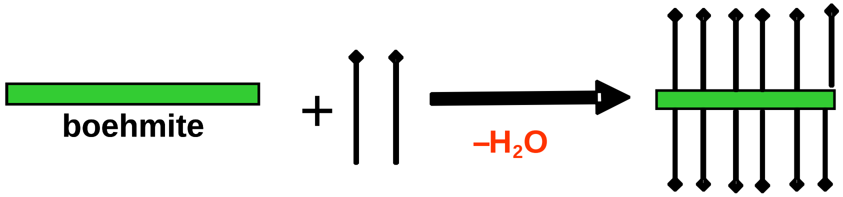
- **Organic corrosion inhibitors are widely used in liquid applications (boilers, recirculating cooling lines, etc.), but not in coatings**
- **Corrosion inhibitors must**
  - Have limited solubility in organic solvents and some but not excessive solubility in water,
  - Have an effective specific gravity of ~2 to 5
  - Have and absence of deleterious effects on coating's mechanical properties (e.g. plasticization) and most importantly they must not interfere with the curing process
- **Unfortunately, most organic corrosion inhibitors have low specific gravities and reactive groups.**
- **Nanostructured materials are good carriers for organic corrosion inhibitors**

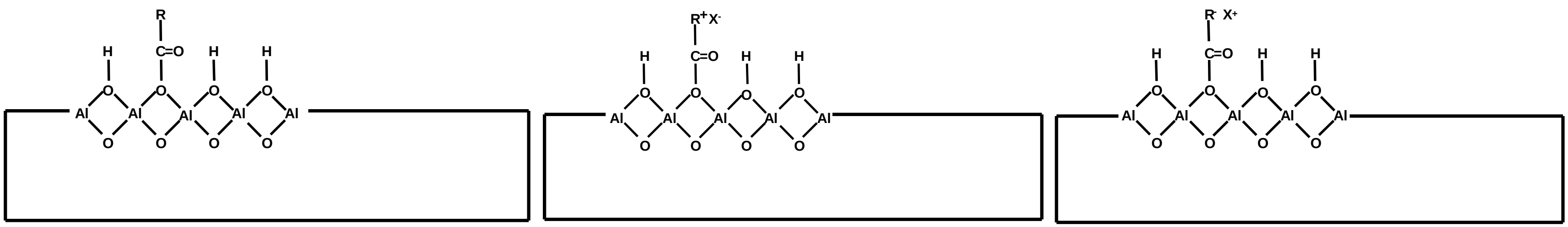
Types of Nanostructured Carriers



Boehmite Nanoparticle Carriers

Nanoparticle Carrier





R= imidazole, triazole, benzothiazole, etc.

R^+ = protonated or quaternary amine

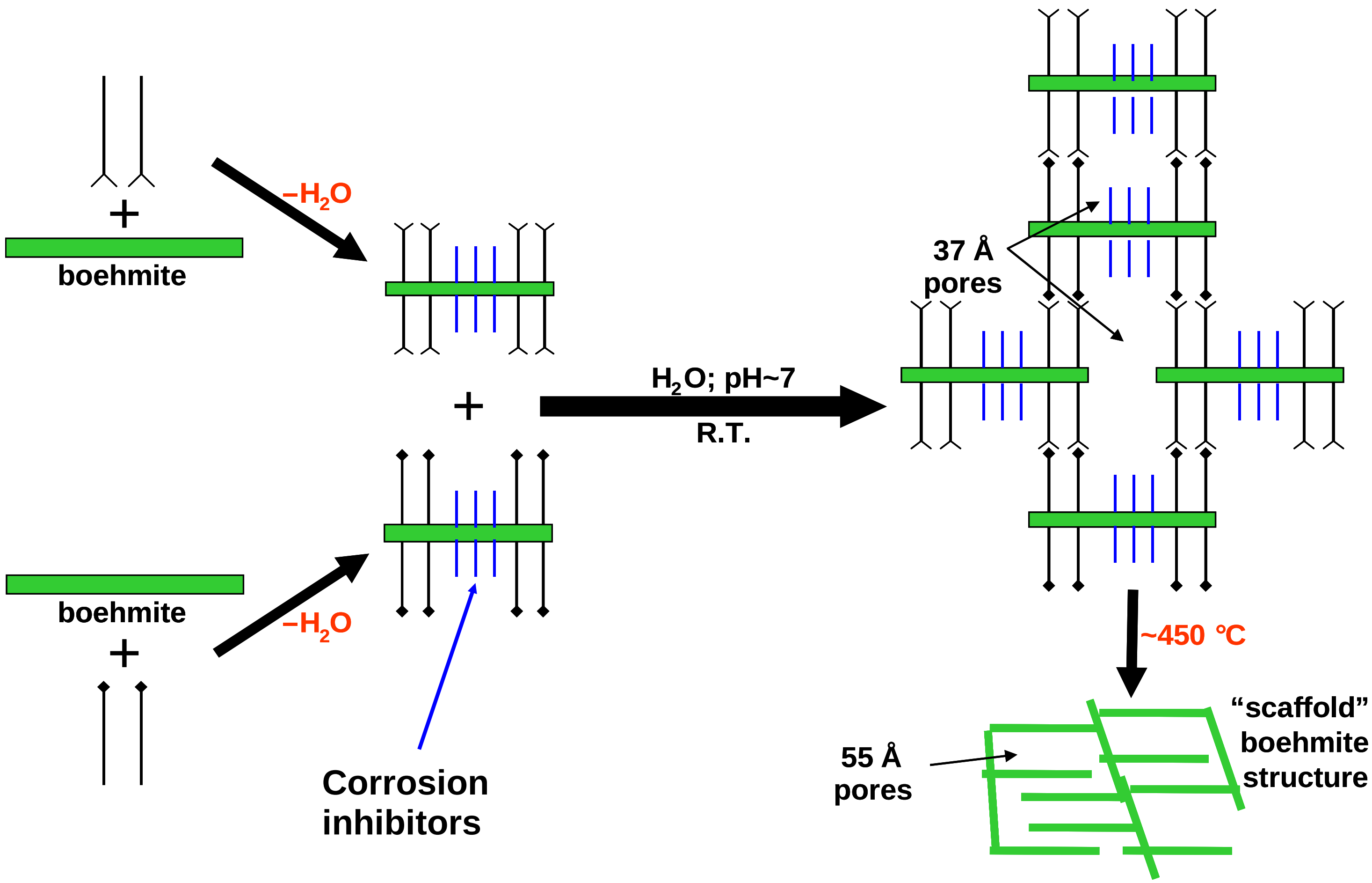
X^- = organic anion or inorganic anion

R^- = carboxylate

X^+ = organic cation or inorganic cation

Nanoparticle carriers release corrosion inhibitors by both ion exchange and by pH triggered release

Nanostructured Boehmite Carriers



Nanostructured Boehmite Carriers Properties

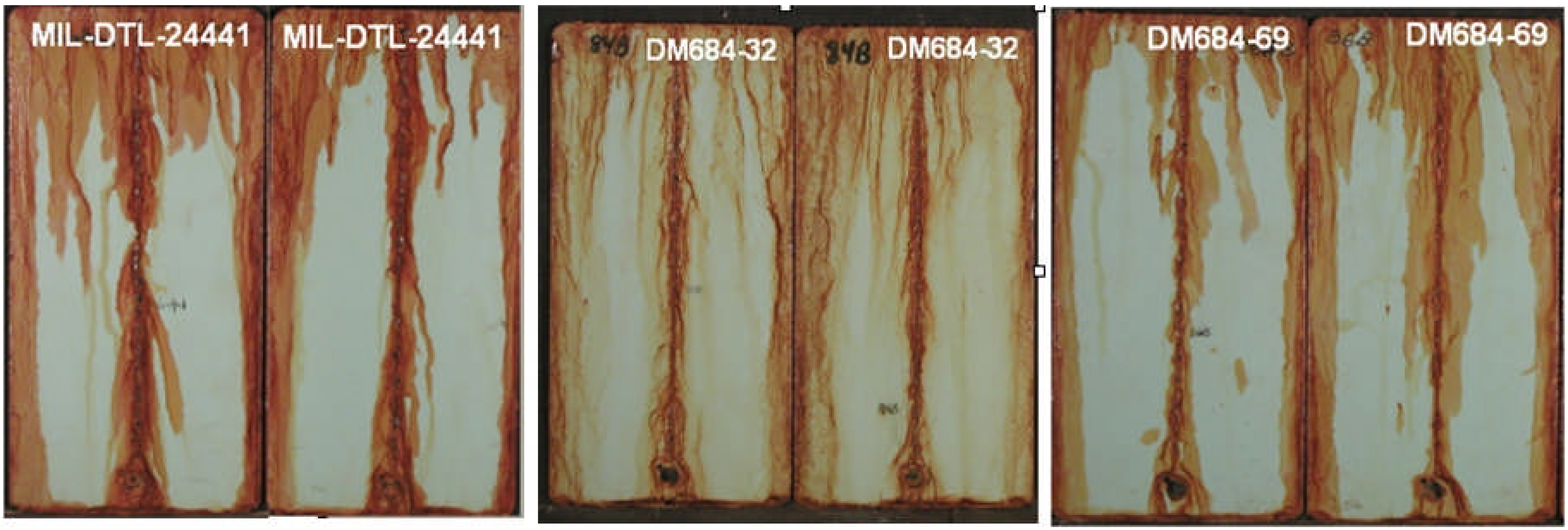
- **Pores are accessible to water without organic burnout**
- **Surface area of 260m^2/g**
- **Tunable hydrophobicity**
- **Nanoporous carriers can be prepared without corrosion inhibitors and then be filled with inhibitors later**
- **“Burned out” nanostructures can also be filled with corrosion inhibitors**
- **Release rate controlled by pore size and pore hydrophobicity**

Inhibition Examples

Coating Formulation

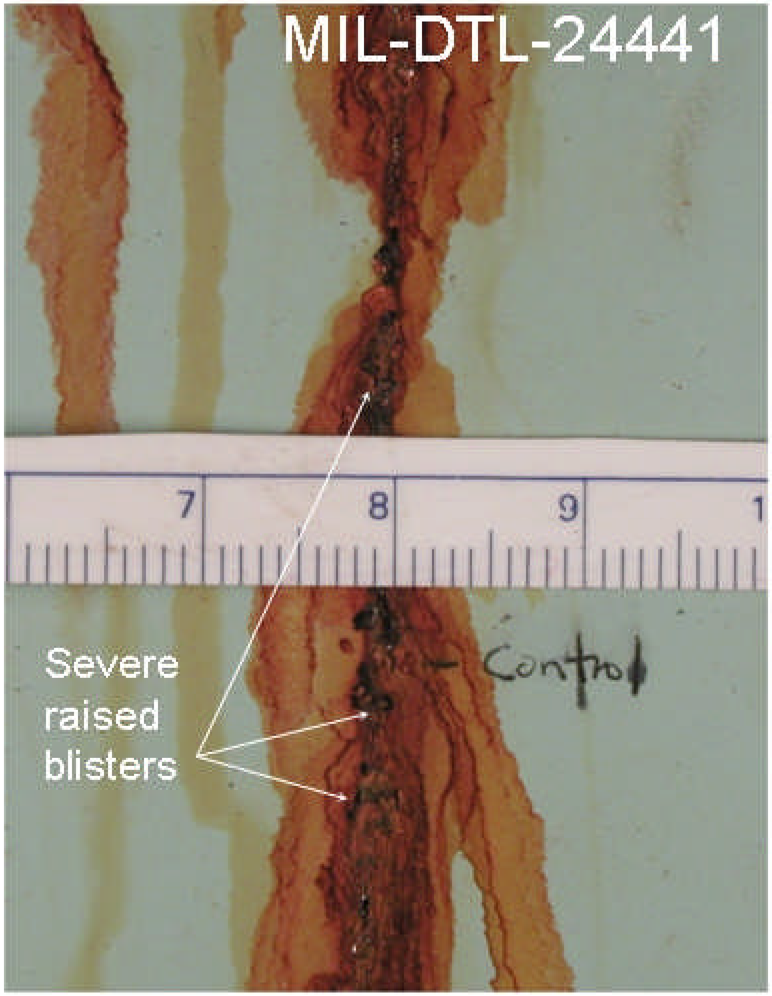
- Nanomaterials incorporated in to MIL-DTL-24441/20A formula
- Applied using HVLP spray gun to blasted steel panels
- Coatings had good sprayability and film quality
- Coating corrosion resistance performance evaluated by salt fog testing (ASTM B-117)

Corrosion Testing



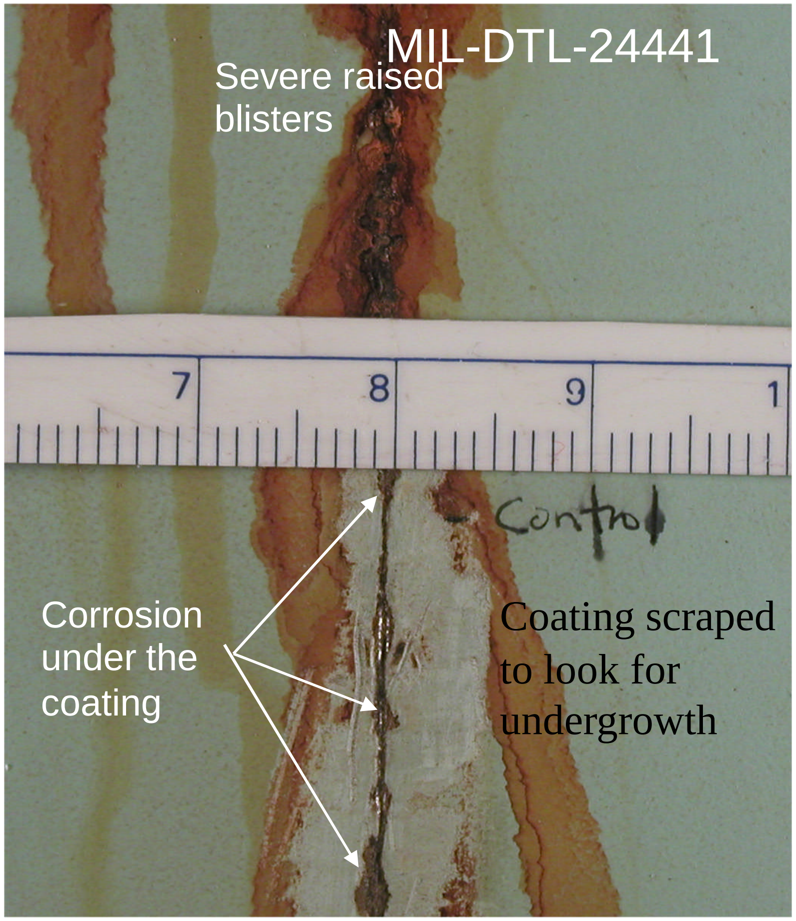
After 500 hrs salt fog testing TDA nanoparticle coatings (center and right) have less corrosin overgrowth than standard coating (left)

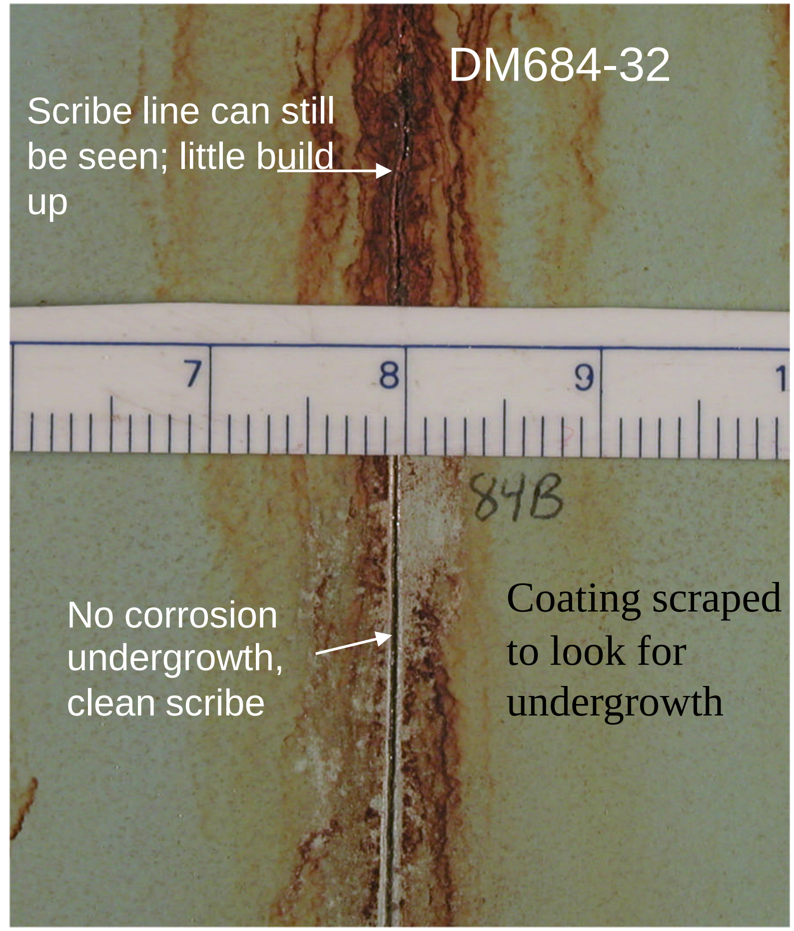
Close up of Scribe



Smart coating dramatically reduced blistering and corrosion build up in scribe

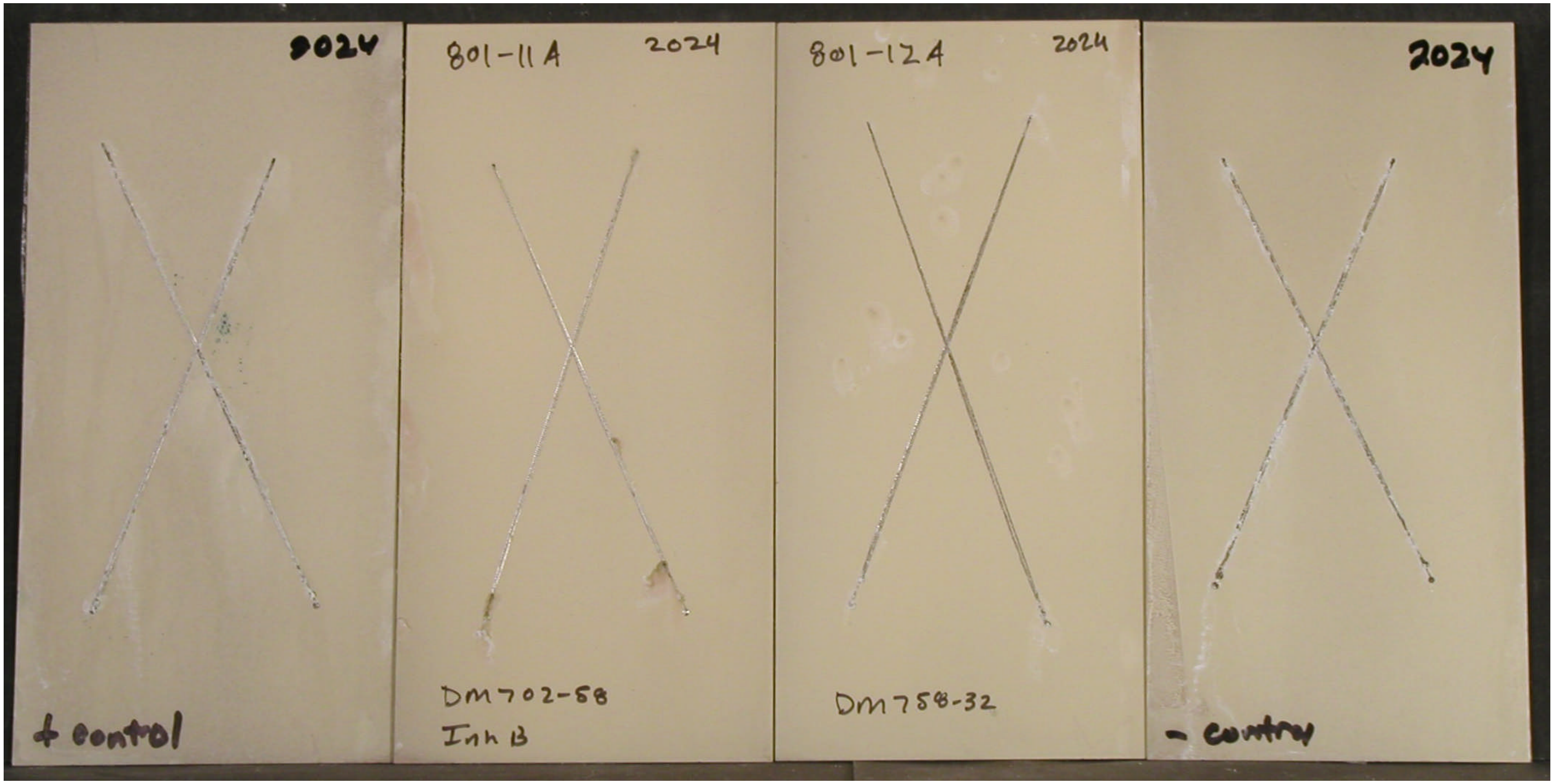
Rust/corrosion removed (in bottom half of panel) to look for undergrowth





- **Corrosion undergrowth in Coating MIL-DTL-24441**
  - **No corrosion under coating with TDA Coating**

Nanostructured Corrosion Inhibitors



Photographs of modified 23377 Coatings over AA2024 panels. Left to right (2000 hours); Non-chrome corrosion inhibitor control, Nanostructure w/ mixed inorganic/organic inhibitor, Nanostructure w/ computer identified organic inhibitor and negative control.

Summary

- **Nanoparticles and nanostructures can serve as excellent carriers for inhibitors**
- **Organic inhibitors, inorganic inhibitors and mixed inhibitor carriers are possible**
- **Controlled and triggered release can be built in**