Non-Toxic Anti-Corrosives: Selection, Formulation, & Qualification

PACIFIC NORTHWEST SOCIETY FOR COATINGS TECHNOLOGY

Vancouver – BC Section
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COMPETENCE IN COLOR

Agenda

- Heubach GmbH – Heucotech Ltd Background:
- Corrosion – *Briefly*:
  - Definition
  - Corrosion Cell Diagram
- Non-Toxic Anti-Corrosives:
  - Definition
  - Toxic versus Non-Toxic
    - Mechanisms
  - Selection
  - Formulation
  - Qualification

Heubach GmbH / Heucotech Ltd Background

3 Main Production Facilities

The Heubach Group is fully owned by the Heubach Family

North America	Europe	Asia / Pacific	
Heucotech Ltd. Fairless Hills, PA, USA	Heubach GmbH Langelsheim, Germany	Heubach Colour Pvt. Ltd. Ankleshwar, India	Hangzhou Heubach Pigment Co., Ltd. Hangzhou, China

Heubach GmbH / Heucotech Ltd Background

GROUP STRUCTURE & FUNCTIONAL OVERVIEW

Heubach Europe

- Headquarters of the Heubach Group
- Production Hub for Inorganic Pigments, Specialities, anticorrosive pigments, Pigment preparations for EMEA

Heubach India

- Production Hub for Organic Pigments
- Pigment preparations for India/Asia

Heubach NAFTA

- Pigment preparations for Americas

Heubach China

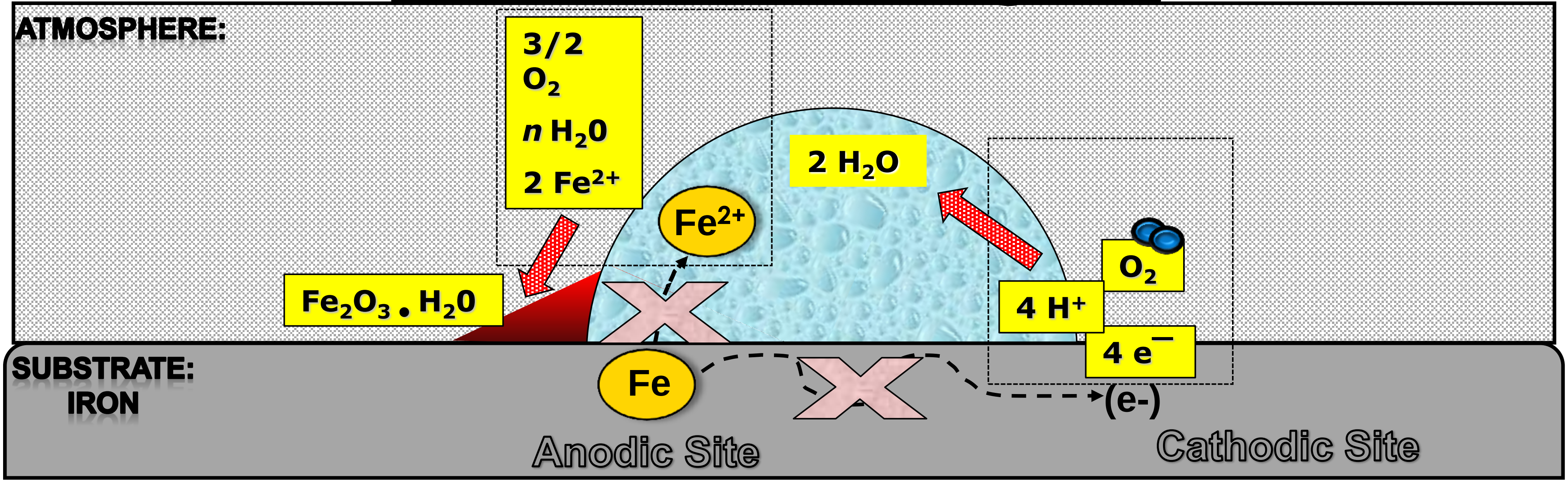
- Production of Inorganic Pigments under consideration
- Production of preparations for China/Asia under consideration

Corrosion is Everywhere !

Corrosion is Everywhere ! – Especially in the Midwest !

Definition of Corrosion: The electrochemical deterioration of a metal due to the reaction with its environment involving the oxidation of a metal and the reduction of another material.

Corrosion Cell Diagram



Electron Conductor:	Metal
Ionic Conductor:	Water
Electron Acceptor:	Oxygen

Non-Toxic Anti-Corrosives: Definition

- The definition can vary depending on who you are talking to, due to changing laws & the globalization of our industry (e.g. – European Directive concerning zinc containing compounds).

- In NAFTA regions, "Non-Toxic Anti-Corrosives" are generally considered anti-corrosives which are chrome free & lead-free or *extremely low lead containing*.

- Zinc has come under scrutiny primarily because of EU Directive mandating suppliers to inform their customers of the level of zinc (dust, flake, or Zn^{+2} form) within their product, when selling or transporting within an EU Country. Zinc is a *potential* aquatic toxin.

- Some municipalities within North America have restrictions on the amount of zinc which can be contained within their effluent water. Outside of these municipalities, or customers selling into EU Countries, there is not a big push within North America to formulate away from zinc containing compounds.

Non-Toxic Anti-Corrosives: Toxic versus Non-Toxic

Lead Based Anti-corrosives - Lead Acid Reaction (Soap Formation): Indirect

$PbO + n\text{-}C_8H_{17}COOH \rightarrow n\text{-}C_8H_{17}COO^{-}Pb^{+}$

Pelargonic Acid → Lead Pelargonate

Chrome (Cr+6) Based Anticorrosives - Oxidative Nature: Direct

Solubility: Cr+6 > Cr+3. Chromate ions are easily leached out and can be transported to defect sites within the coating.

Passivation: Cr+6 is a very strong anodic passivator. Adsorbing Cr+6/+3 Species stifle the O2 reduction reaction. This reaction will proceed regardless of the PVC of the coating. Cr+6/+3 species are not expended easily and can easily passivate & 're-passivate' the substrate in question.

Inorganic Non-Toxic Anti-Corrosives - *Typically*, Non-Oxidative Nature: Direct

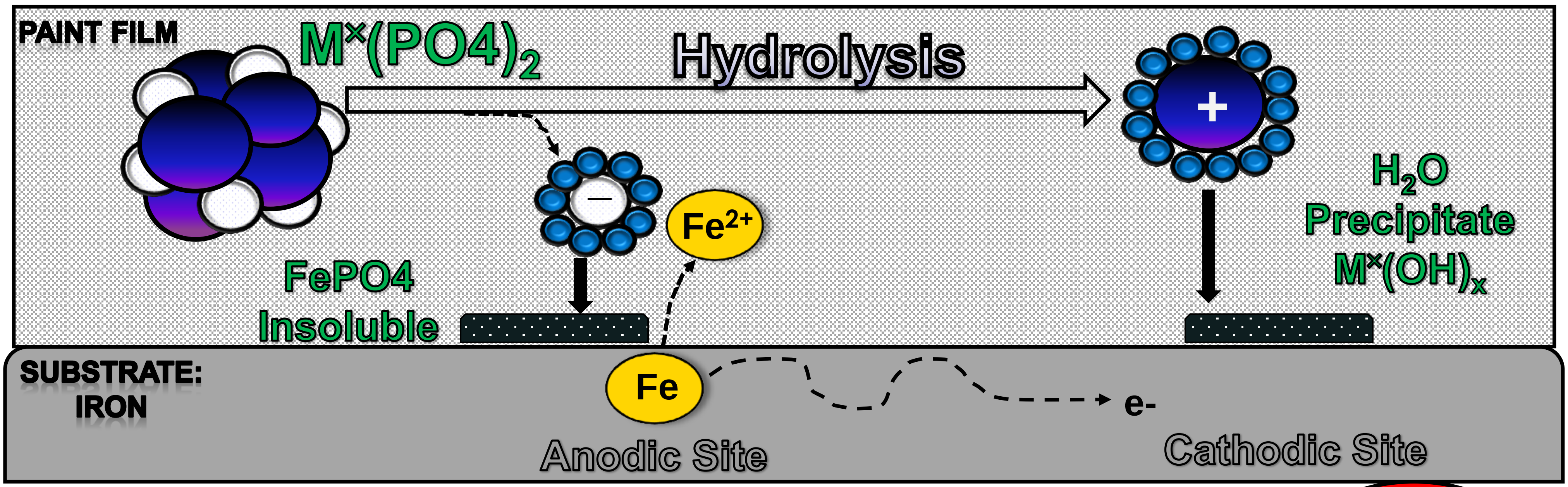
The soluble ions of the anti-corrosive pigment are inhibitive in nature and do not typically require a reaction with the resin to be effective.

Solubility: Will vary depending on the metal cations complexed with the anionic carrier.

Passivation: Primarily anodic passivators. Passivation strength will vary between complexes used. Performance is related to PVC, *or solubility of the complex within the coating*. Typically, more soluble complexes are expended faster within the coating.

<u>Inorganic</u> Non-Toxic Anti-Corrosives - *Typically*, Non-Oxidative Nature: Direct

Passivation Mechanism -



Non-Toxic Anti-Corrosives: Toxic versus Non-Toxic

<u>Organic</u> Non-Toxic Anti-Corrosives - *Typically*, Non-Oxidative Nature: Direct

The soluble ions of the anti-corrosive pigment are inhibitive in nature and do not typically require a reaction with the resin to be effective.

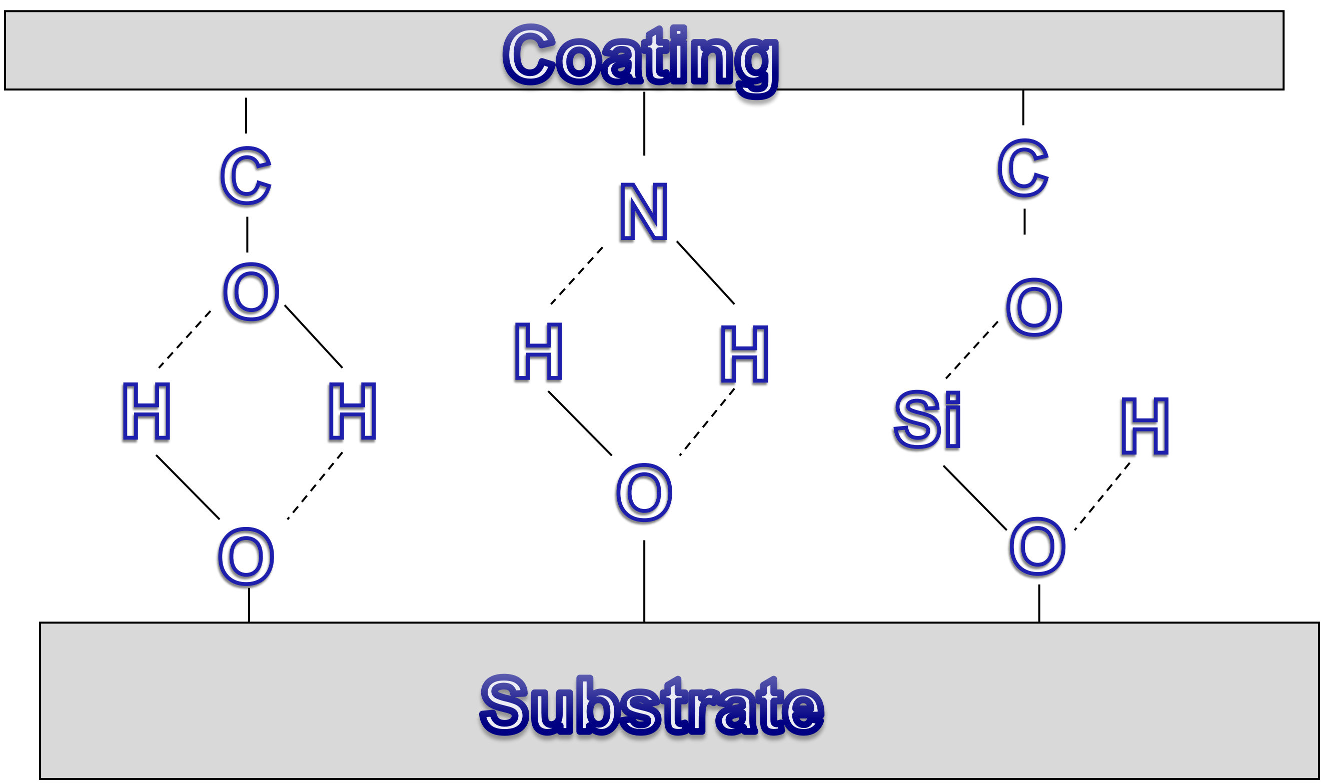
Solubility: Will vary depending on the organic complex used. Typically more soluble than the inorganic anti-corrosives, as most are organic salt complexes.

Passivation: Primarily anodic passivators. Many will act as adhesion promoters, as well. Passivation strength will vary between complexes used. These are very effective at low loading levels & migrate quite readily to defect sites with the coatings. Most often are used in combination with an inorganic anticorrosive.

Non-Toxic Anti-Corrosives: Toxic versus Non-Toxic

<u>Organic</u> Non-Toxic Anti-Corrosives - *Typically*, Non-Oxidative Nature: Direct

Passivation Mechanism



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<u>Organic</u> Non-Toxic Anti-Corrosives - *Typically*, Non-Oxidative Nature: Direct

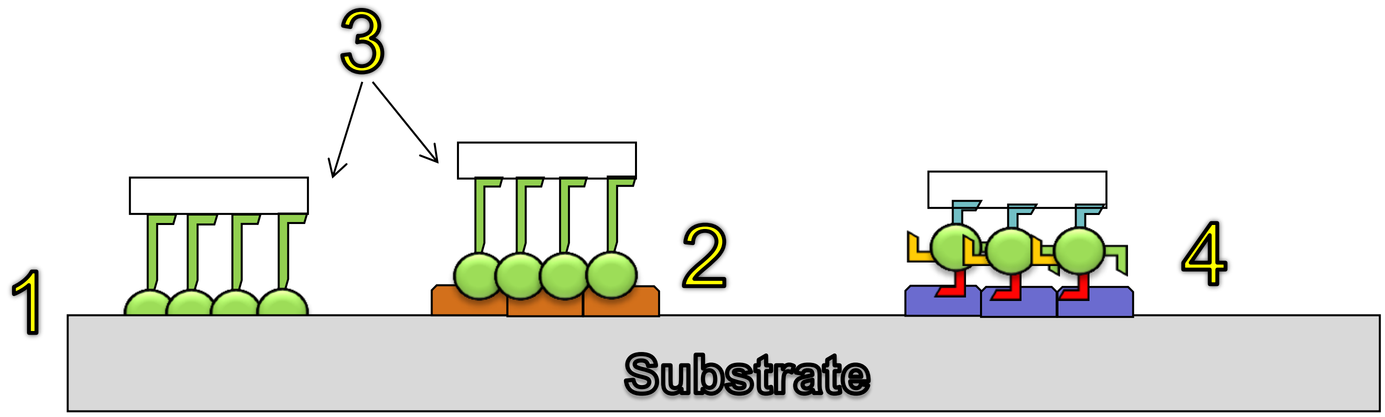
Passivation Mechanism - Multifunctional

1. Improved Adsorption to the substrate or primer. Protective layer formation / Improved wet adhesion.

2. Improved Anodic Activity: Formation of insoluble complex salts at anodic defect sites.

3. Improved Barrier Activity: Act to reduce permeability & porosity in the coating. Reduce propensity to blister.

4. Improved Cathodic Activity: Formation of precipitates due to increased alkalinity at cathodic sites.



<u>Inorganic + Organic</u> Non-Toxic Anti-Corrosives - *Typically*, Non-Oxidative

Nature: Direct

USING SYNERGIES

Inorganic Anti-Corrosive Pigments

- Modified orthophosphates
- Modified polyphosphates
- Modified orthophosphate silicates
- Modified polyphosphate silicates
- Zinc phosphate
- Calcium modified silica

Organic Anti-Corrosive Inhibitors e.g.

- Zinc salt of 5-isonitrophthalic acid
- Zinc salt of cyanuric acid
- Zinc salt of phthalic acid
- Succinic acid derivates and their amine salts
- Metal salts of dinonylnaphthalene Sulfonates
- Dinonyl naphthalene sulfonates

1. QUALITY

2. CONSISTENCY

3. PHYSICAL PROPERTIES

1. QUALITY

- Can be overlooked by the formulator when choosing a non-toxic anti-corrosive pigment.
- Not all anti-corrosives are the same.
- Be Aware - It is possible for the introduction of undesireable heavy metals into your coating (e.g. - Pb, As, etc). If the anticorrosive supplier does not carefully scrutinize their raw materials it is possible for their end product(s) to contain *higher than trace amounts* of certain heavy metals.
- Certain components of anti-corrosive pigments are hygroscopic and their performance can change over time.
- Demand a C of A with each sample/shipment.
- If you have the means, have the anticorrosive tested for metals content..

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2. CONSISTENCY

- If the anticorrosive supplier does not carefully regulate their manufacturing processes, anticorrosive properties can vary from lot-to-lot.
- Every anti-corrosive manufacturer has a proprietary process for which they manufacture anti-corrosives, generally involving a ***reaction*** step followed by a ***classification*** step. If these processes are not regulated, lot-to-lot variations can exist with any given anti-corrosive.
- Demand a C of A with each sample/shipment.
- Demand various lots for testing, from the supplier, for any given anti-corrosive.

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3. PHYSICAL PROPERTIES

- **Solubility**: Performance is related to the solubility of the anti-corrosive complex in a given coatings system. The solubility of the anti-corrosive complex will vary depending on the metal cations used to complex with the anionic carrier. (i.e. - $M^x(PO_4)_2$ M: Zn, Al, Ca, Sr, Mg….).

- **pH:** Can influence the end performance/stability of any given coatings system. pH is often dictated by the anionic carrier used.

- **Oil Absorption (OA):** OA's are related to CPVC (critical pigment volume concentration) for any given coating system. Pigment OA's can be used to calculate a CPVC for any given coating system:

  - $$\text{CPVC} = \frac{1}{\left(1 + \dfrac{[V_a \times OA_a \times \rho_a + V_b \times OA_b \times \rho_b + V_c \times OA_c \times \rho_c]}{93.5}\right)}$$

  - It is believed the optimal range for formulating coating systems for anti-corrosive properties is at a PVC/CPVC Ratio of (0.30 - 0.70)

- **Particle Size Distribution(PSD):** EXTREMELY Important for Pigment Packing!!

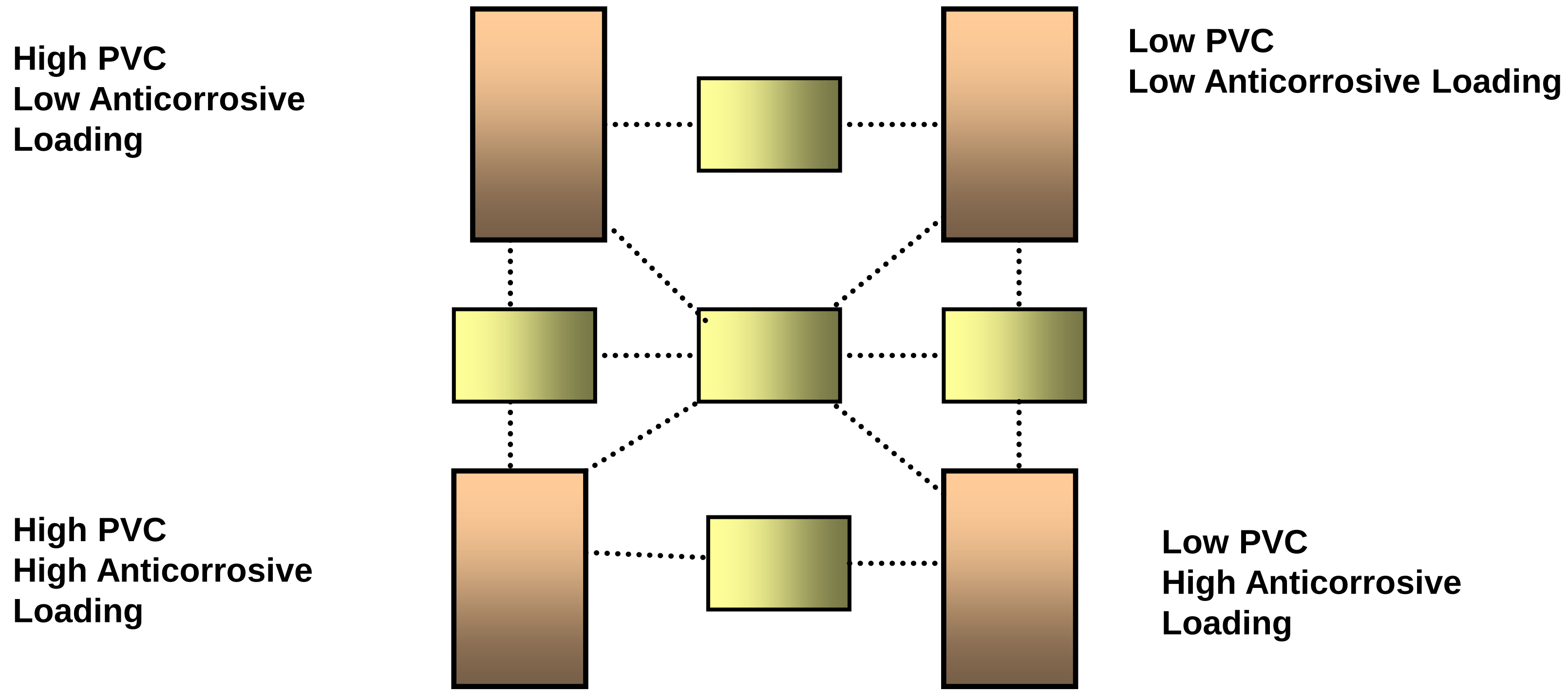
3. PHYSICAL PROPERTIES

continued

- **Particle Size Distribution(PSD):**
  - There are various ‘schools of thought’ on what is the optimal anti-corrosive pigment PSD for formulating anti-corrosive coatings.
  - We believe the optimal average particle size for any given anti-corrosive pigment to be in the range of 2.0-4.5 microns, with a uniform PSD.
    - At this average particle size range with a uniform PSD, functionality of the anti-corrosive complex is optimized.
    - At this average particle size range with a uniform PSD, minimal effort is needed to attain a GOOD grind (i.e. – +6 NS Hegman)
  - Both the ***reaction*** step & the ***classification*** step, discussed earlier, are critical in the anti-corrosive manufacturing process.

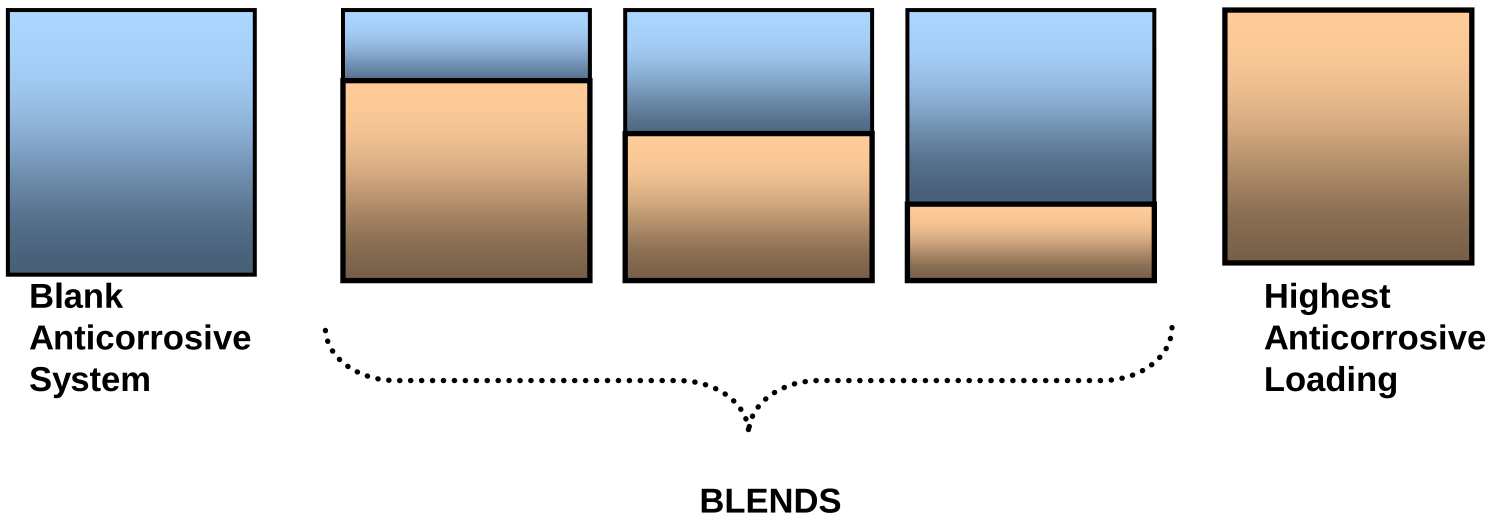
Formulating Recommendations:

1. Start by considering the PVC of your formulation. Is it optimized? If not, perform a PVC/anti-corrosive loading level ladder study with your formula & anti-corrosive.



Formulating Recommendations (continued):

2. If you have gloss requirements, and/or you feel the PVC of your system is optimized, simply run a loading level ladder study with the highest recommended level of anti-corrosive in question and a 'blank' system.



Formulating Recommendations (continued):

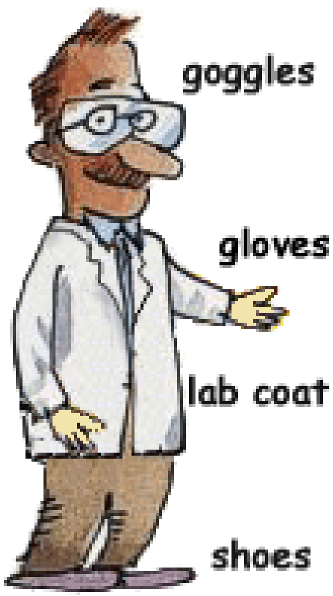
3. Other factors to consider.
    - **Extender Pigments** – Platy or lamellar shaped extenders are typically the best for formulating corrosion resistant systems.
    - **Other additives in your system**. It is best to minimize the level of hydrophilic additives in corrosion resistant formulas.
    - **Explore synergies between anti-corrosives (ie.- Inorganic / Organic Anticorrosives).** Organic Anticorrosives are functional at very low loading levels & work best when used in combination with an Inorganic Anticorrosive.
4. Anti-corrosives have different physical characteristics & should not typically be tested on a direct weight replacement for another anti-corrosive.

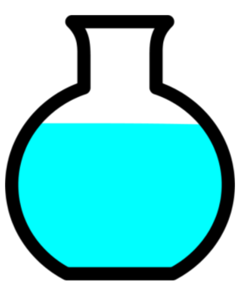
- There are various methods used to qualify coatings for corrosion resistance.
  - **Static Testing**
    - Salt Spray Testing. Not exactly real world testing, but many companies still want to see how their coating will fare in this test.
  - **Cyclic Testing**
    - Prohesion Testing / QUV-Condensation-Prohesion Testing / Xenon Arc Testing. More *realistic testing* as it incorporates different cycles of testing.
  - **Electrochemical Testing**. Data can be gathered quicker than either static or cyclic testing. Interpretation of the results can be difficult depending on the method utilized.
    - Rest Potential Analysis
    - Direct Current Analysis
    - Electrochemical Impedance Spectroscopy (EIS)
    - Electrochemical Noise Analysis
  - **Real World – Exterior Exposure**. Can take months or years to gather usable data.

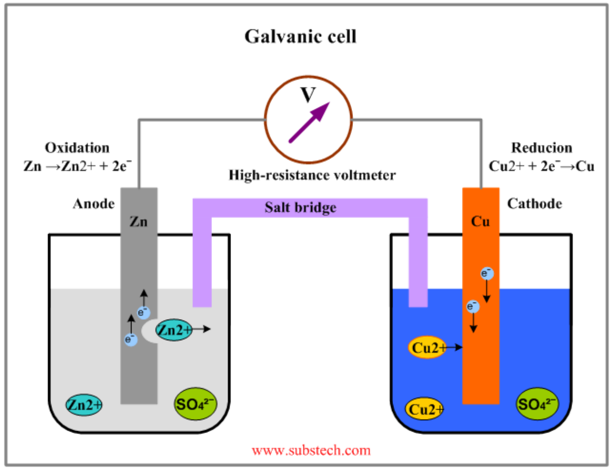
- Whatever the test method you choose to qualify, make sure the method *fits* and is representative of the environment the coating will be exposed to.

- Oftentimes, the test method will be dictated by your end customer.

- Consult the Experts on what various test methods you can employ.







Thank You!

Heucotech Ltd – Heubach GmbH

Andrew Thorn – Technical Marketing Manager, Anticorrosives

Email: Andrewthorn@heubachcolor.com

Office phone: 215.736.0712 ext.157

Cell phone: 219.776.6602