

## NEW CHROMATE-FREE CORROSION INHIBITING ADDITIVES USED IN COATINGS

Tony Gichuhi, PhD

*ICL Specialty Products  
St Louis, MO*

### Abstract

Zinc phosphate is widely accepted as a nontoxic material that could provide adequate corrosion protection to coatings under demanding corrosive environments. Recently, the rising cost of zinc, however, has forced formulators to look for less expensive and suitable functional offsets. Nowhere has the challenge of formulating protective coatings systems with nontoxic materials been greater than in the general industrial maintenance segment where the toxic counterparts such as chromates remain relatively cheap and difficult to replace with phosphates and other benign products. This paper will address the concerns of finding suitable cost-effective zinc phosphate alternatives that meet corrosion requirements and at the same time leave no environmental footprint. Corrosion inhibitors provide an indispensable function to protective coatings. The performance of a coating under corrosive conditions requires that the inhibitor provide sustainable protection during the coating's lifetime. The growing pressure to find less expensive, effective zinc phosphate offsets has shifted the coatings pendulum to more eco-friendly alternatives. This paper captures specific products reflecting the new paradigm of products based on heavy-metal free chemistry as well as lower zinc containing products.

### Introduction

The price of zinc has gone up 242 percent in the last year, based on London Metal Exchange (LME) numbers (1). This skyrocketing price of zinc over the last two years has undoubtedly forced many formulating chemists to find suitable alternative anticorrosive products with less of the metal. The rising price of zinc set off a chain reaction in paint formulations based on zinc phosphate anticorrosive pigments, where prices went unabated. Formulators were demanded to re-evaluate the paints to cut costs wherever possible. In an effort to capitalize on the growing demand of cheaper alternative pigments, research was spawned to develop anti-corrosive pigments less reliant on zinc and more dependent on other important properties such as morphology, barrier function, ion scavenging and exchange, non-oxygen dependence, enhanced alkalinity, improved compatibility with binder systems, and better particle size distribution. Traditional zinc phosphate pigments are composed of zinc and phosphate ions existing as an ionic complex salt  $Zn_3(PO_4)_2 \cdot 2-4 H_2O$ . Various forms of zinc phosphate otherwise known as modified zinc phosphates exist in the market today. Several distinguishing traits of  $Zn_3(PO_4)_2 \cdot 2-4 H_2O$  include the stoichiometry of zinc and phosphate ions whereupon the zinc ions generally make up 50-60 wt% and phosphates 40-50%. Other modifications include surface treatments with various organic compounds (amino silanes, epoxy silanes, carboxylic acids, etc), which serve to increase the inhibition efficiency of zinc

phosphate by controlling its solubility, pH, dispersion, and oil absorption. Modifications containing fillers and other inhibitive oxides (strontium, barium, molybdenum, calcium, and zinc) are also quite common and have been shown to offer system specific performance improvements in select binder systems. For example, in alkyds, basic auxiliary pigments such as zinc oxide and magnesium oxide were found to provide unique synergy with zinc phosphate. Basic oxide contents need to be high. A 20:1 zinc phosphate to calcium oxide ratio gave performance in a linseed oil alkyd equivalent to that of red lead/linseed oil (2). On the other hand it was possible to replace a great deal of zinc phosphate volume with basic auxiliaries at some cost savings. An example is a high solids alkyds, where the zinc phosphate was modified with a surface treated calcium silicate (3). The paper highlights research efforts to find less expensive alternatives to zinc phosphate which give adequate corrosion resistance for typical general industrial and light duty applications. Two products will be highlighted. The first is a heavy-metal free, zinc-free product referred to as Hybrid A and the second is a low zinc-containing anticorrosive pigment referred to as H-300. H-300 is a cost-effective zinc phosphate-type inhibitor designed to compete head-to-head with other zinc phosphate and modified zinc phosphate corrosion inhibitors. With rising raw material costs, the brief refresher of the mechanisms of both toxic and nontoxic corrosion inhibitors remains essential in understanding and devising cost effective, high performance, protective coatings.

### Chromates: Toxic corrosion inhibitors

#### *Anodic and Cathodic Passivation*

Chromate-based corrosion inhibitors have traditionally been used in the coatings industry to prevent corrosion. Chromate type inhibitors can broadly be classified as strongly oxidizing inhibitors based on oxymetal anions of hexavalent chromium Cr<sup>6+</sup> namely CrO<sub>4</sub><sup>2-</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> with their complementary cations (Sr<sup>2+</sup>, Ba<sup>2+</sup>, Ca<sup>2+</sup>, Zn<sup>2+</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>) providing a wide range of solubilities needed to cover the large variety of vehicles and binders used for corrosion primers. Besides being effective anodic inhibitors, chromate salts, particularly trivalent chromium, Cr<sup>3+</sup>salts functions as an effective cathodic inhibitor under alkaline conditions. The solubility of the most common chromates used as corrosion inhibitors are shown in Table 1 below.

Table 1: Solubility of Chromate Corrosion Inhibitors

Chromate salts	Solubility in water moles/liter [g/l]	Comments
NaCr <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O	3.3 [908]	Solubility too high for a pigment (Used as flash rust inhibitor)
3ZnCrO <sub>4</sub> ·K <sub>2</sub> CrO <sub>4</sub> · Zn(OH) <sub>2</sub> ·2H <sub>2</sub> O	0.015 [13.1]	Zinc yellow. OK solubility (Used as corrosion inhibitor)

SrCrO <sub>4</sub>	0.007 [1.4]	Solubility OK for pigment (Used as corrosion inhibitor)
ZnCrO <sub>4</sub> .4Zn(OH) <sub>2</sub>	0.0003 [0.17]	Solubility OK for pigment (Used as corrosion inhibitor)

The remarkable performance of chromate-based inhibitors in high performance coatings (e.g. coil coating, wash primers, aerospace, and automotive coatings) has made them quite difficult to replace with nontoxic chemistries. None of the nontoxic corrosion inhibitors provide the universal appeal of chromate salts at the same cost and dosage level. Besides being effective anodic and cathodic inhibitors as exemplified by the following equations, chromate corrosion inhibitors are equally important in surface pretreatments for metal where corrosion resistance and coating adhesion is critical.

Table 2: Mechanisms of Chromate Corrosion Inhibitors

Substrate	Protective Mechanism: Anodic & Cathodic
Ferrous	<p><u>Cr<sup>6+</sup> as anodic inhibitors</u>  <math>2\text{CrO}_4^{2-} + 6\text{FeO} + 2\text{H}_2\text{O} \rightarrow \text{Cr}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + 4\text{OH}^-</math>            Tenacious oxide film formed at anodic sites stops further Dissolution of metal</p> <p><u>Cr<sup>3+</sup> as cathodic inhibitors</u>  <math>\text{Cr}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Cr}(\text{OH})_3 + 3\text{H}^+ \rightarrow \text{Cr}_2\text{O}_3 \cdot 3\text{H}_2\text{O}</math>            Precipitate impedes cathode reactions (oxygen reduction)</p>
Zinc	<p><u>Cr<sup>6+</sup> as anodic inhibitors</u>  <math>3\text{Zn} + 2\text{CrO}_4^{2-} + 5\text{H}_2\text{O} \rightarrow 3\text{Zn}(\text{OH})_2 + \text{Cr}_2\text{O}_3 + 4\text{OH}^-</math></p>
Aluminum	<p><math>\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^-</math>; <math>\text{Al}^{3+} + 2\text{H}_2\text{O} \rightarrow \text{AlOOH} + 3\text{H}^+ + 3\text{e}^-</math>;  <math>\text{Cr}_2\text{O}_7^{2-} + 8\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}(\text{OH})_3 + \text{H}_2\text{O}</math></p>

The so-called chromate conversion coating (CCC) is exemplified in Figure 1 below. The high solubility of chromate leachates allows rapid migration to defect sites in the coating to repair the oxide layer, deposit a passive layer, and prevent further corrosion. This process is often referred to as a self-healing mechanism. The self-healing mechanism combines anodic passivation and cathodic passivation of hexavalent chromium and trivalent chromium,

respectively. Chromate conversion coatings are used on metals such as aluminum, magnesium, cadmium, and steel. They provide good corrosion resistance and are “self-healing” in the sense that they can spontaneously repair small amounts of chemical and mechanical damage. Self healing originates with a reservoir of soluble Cr(VI) species located in the outer layer of a mainly Cr(III) hydrated oxide/hydroxide coating.(4) Upon contact with an electrolyte, the labile Cr(VI) s released into solution and transported to damaged areas here it is reduced and precipitated to form an insoluble Cr(III) hydroxide barrier (5-6)

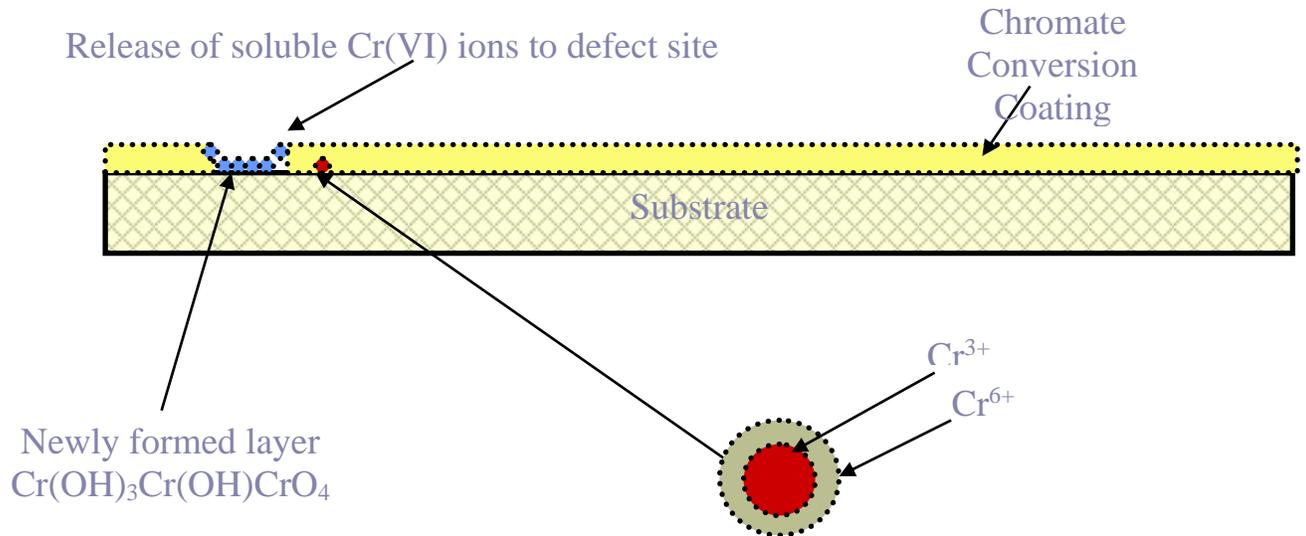


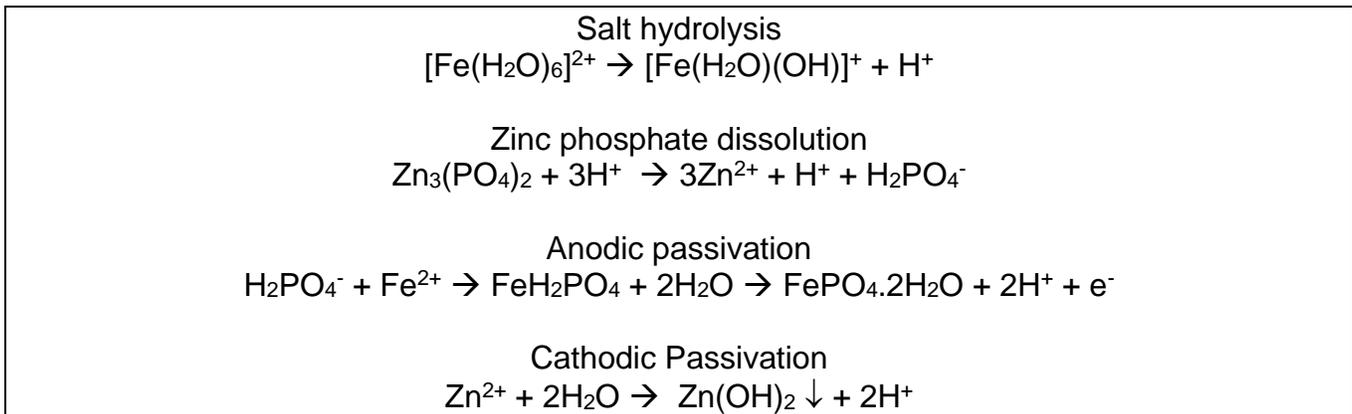
Figure 1: Self-Healing Mechanism of chromate corrosion inhibitor

## Zinc Phosphate: A non-toxic corrosion inhibitor

### *Anodic and Cathodic Passivation*

Zinc phosphate controls corrosion in neutral solutions by acting as a polarizing agent to slow the three elements of the corrosion process: anodic reactions, cathodic reactions, and ionic currents in the solution and the metal itself (7). The dissolution of zinc phosphate through hydrolysis in a coating will result in migration of phosphate and zinc ions to the metal surface whereupon they form a “passive” – protective layer as shown in Table 2. In simple terms, zinc phosphate acts by short-circuiting the electrochemical reactions, which take place during corrosion. As an anodic passivator, it releases phosphate ions, which migrate to the anodic site (8) and zinc ions, which react with the hydroxyl ions generated and forms a precipitate at the cathode.

Table 2: Mechanism of Zinc Phosphate



**Hybrid A: A zinc phosphate alternative**

Hybrid A represents a new generation of environmentally friendly, inorganic zinc-free corrosion inhibitor based on cathodic passivation of calcium phosphate ( $\text{Ca}_3(\text{PO}_4)_2$ ) and a unique selective ion scavenging and exchange mechanism discussed further below. There are major concerns regarding the use of inhibitive pigments containing zinc particularly in Europe. Companies using zinc-based products are required to report yearly emissions of zinc and zinc compounds if their air emissions exceed 200MT/year or releases to water exceed 100MT/year. Zinc can significantly affect local aquatic environments—accumulating in aquatic organisms (but not plants) and poisoning species that consume them (9). Hybrid A was developed to fulfill the need for an effective corrosion inhibitor for waterborne and solvent-borne coatings that could perform equal to or better than typical zinc-based inhibitive pigments. Hybrid A leaves no environmental footprint and is based on constituent components Generally Recognized as Safe (GRAS) for food by the Food & Drug Administration (10).

Hybrid A combines the unique synergistic properties of cathodic passivation and ion scavenging-exchange mechanisms. The typical heavy metal-free inhibitive pigments are effective as anodic passivators in coatings. In other words, they rely on partial solubility to release their corrosion ions (typically phosphate or silicate) in order to impart corrosion resistance to coatings. Hybrid A is an effective corrosive ion scavenger as well as a cathodic passivator. The product does not contain any heavy metals. Instead, it relies on its high porosity to scavenge and adsorb chloride and sulfate ions, thus decreasing their availability to cause corrosion at the substrate. The cathodic protection mechanism is provided by inorganic calcium phosphate salt with extremely low solubility in water. Hybrid A, unlike calcium ion exchange pigments does not exchange calcium ions. Most calcium ion exchange pigments are based on the exchange of cations from a high surface area amorphous alkaline silica gel carrier. Hybrid A does not contain silica or silica gel.

Table 1: Attributes of Hybrid A

Inhibitor	Chemistry	Corrosion Protection	System examples
Hybrid A	Cathodic Passivation/ Ion Scavenging Exchange	Waterborne: <ul style="list-style-type: none"> <li>• Long-term</li> </ul> Solvent-borne <ul style="list-style-type: none"> <li>• Long-term</li> </ul>	Acrylics, Polyurethane, Alkyds, Epoxy, Hybrids (Acrylic Epoxy, Acrylic Alkyds), Water-Reducible Alkyds

The following figure 2 depicts the nature by which Hybrid A acts as an ion scavenging corrosion inhibitor in coating systems. The stratified structure consists of a double-layered mixed metal (Al, Mg) hydrated hydroxide capable of trapping corrosive ions such as chloride or sulfate ions in its matrix and releasing inhibitive alkaline carbonate ions. The carbonate ions can combine with calcium ions to form calcium carbonate or can act as a buffer that maintains the substrate surface at an alkaline pH.

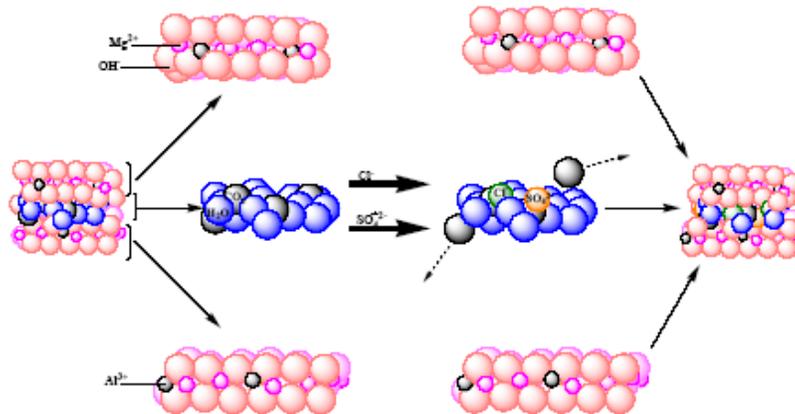


Figure 2: Ion scavenging & exchange mechanism of Hybrid A showing the trapping of chloride and sulfate ions in the host lattice structure

The following examples shown in figure 3-5 illustrate the effectiveness of Hybrid A in enhancing the long-term corrosion protection of water-based acrylic coating with primer and topcoat, water-based acrylic primer only and a solvent-borne coil coating primer-topcoat system. Hybrid A was tested against other zinc-free based inhibitors often recommended as zinc phosphate replacements. The combined synergy of passivation and ion scavenging & exchange mechanism is responsible for the improved performance over the competition. This synergy as one might imagine lends itself well to a variety of coating system under extreme corrosive conditions where chloride and sulfate ions are particularly present. Furthermore, the

layered morphology of the ion exchange pigment underscores the barrier property of Hybrid A which obviously helps in mitigating water transmission through the coating to the substrate.

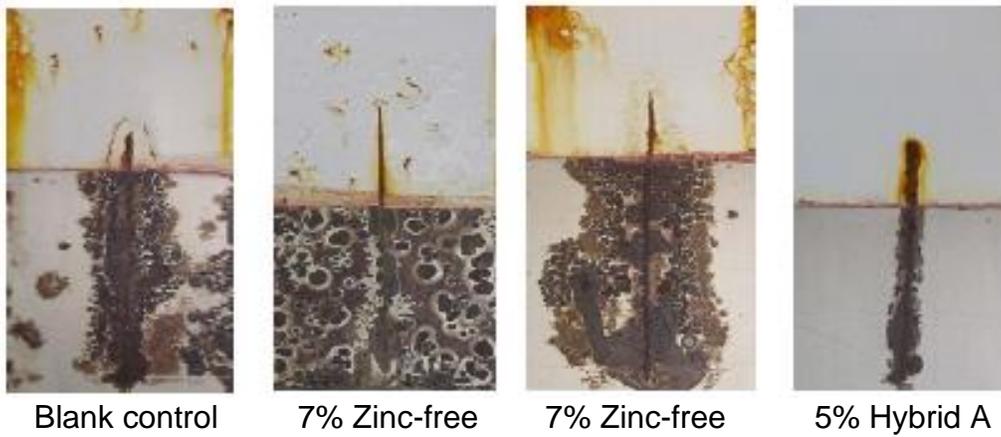


Figure 3: Comparative corrosion resistance of zinc-free inhibitive pigments in a water-based acrylic coating after 336 hours of salt spray (cold rolled steel)

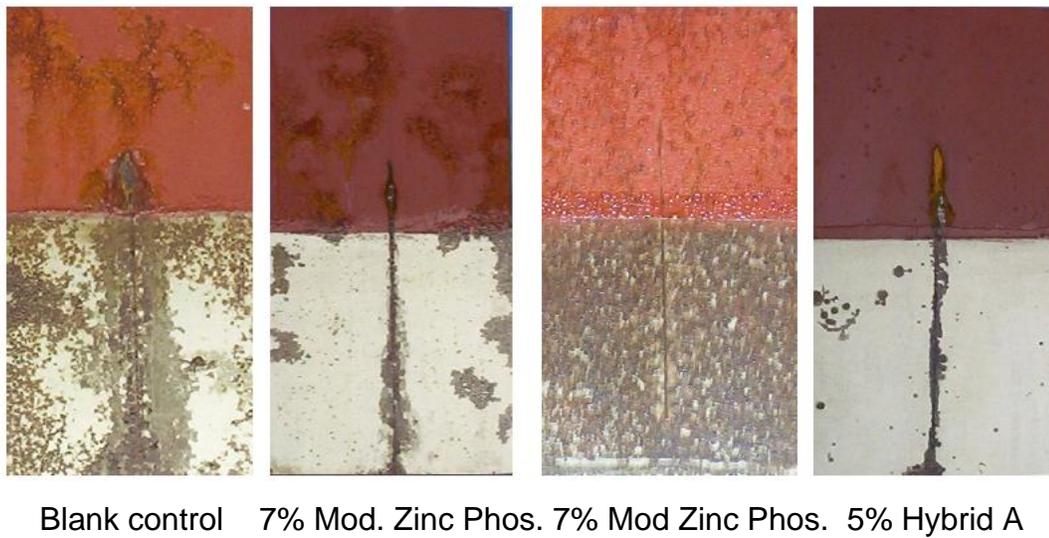
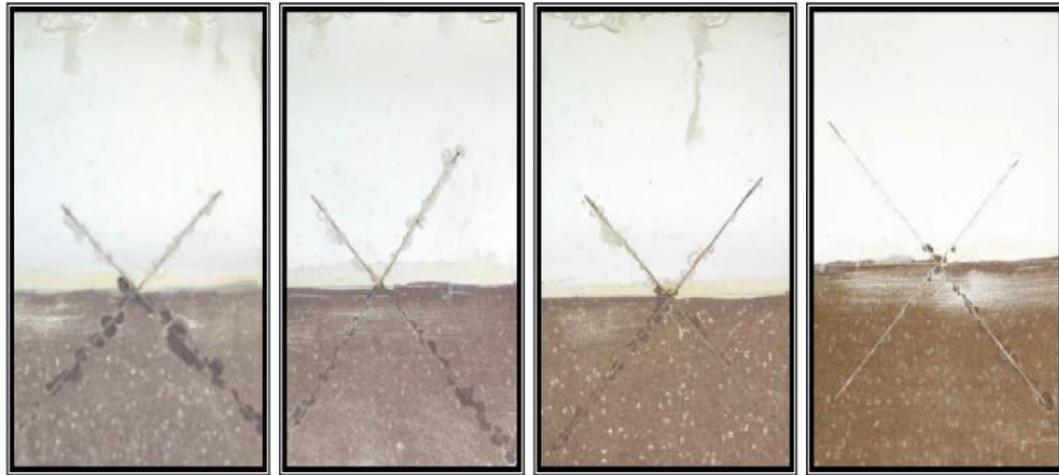


Figure 4: Comparative corrosion resistance vs. zinc phosphate inhibitive pigments in a water-based acrylic coating after 336 hours of salt spray (cold rolled steel)



Blank control    7.5% Hybrid A    7.5% Ca ion exchange 1.4% organic    7.5% Hybrid A 1.4% organic

Figure 5: Comparative corrosion resistance vs. nontoxic commercial calcium ion exchange in a polyester melamine coil coating after 500 hours of salt spray (hot dipped galvanized)

### H-300: A cost effective zinc phosphate alternative

H-300 represents a new, low cost zinc phosphate type inhibitor engineered to provide excellent barrier protection, reserve alkalinity, and enhanced leachability of zinc phosphate. H-300 has a pH closer to 8, which reduces the critical oxygen concentration it needs to passivate metal substrates. As oxygen availability increases, the level of phosphate ion required to achieve corrosion protection decreases. In addition, H-300 contains calcium metasilicate (Wollastonite), which buffers and maintains the alkaline pH in the coating while possessing very slight water solubility. Wollastonite has found increased use in anticorrosive metal primers where its contribution to corrosion resistance and blistering is said to be considerable, especially when employed in surface treated form (11). The wollastonite in H-300 not only lowers the cost of the product but more importantly can be considered an auxiliary synergistic pigment rather than a filler pigment. H-300 contains one-fifth the amount of zinc found in conventional zinc phosphates. Based on this reduced zinc demand, H-300 can be used at the equal loading level as zinc phosphate and maintain superior corrosion performance. Anticorrosive pigments are among the most expensive additives in a given paint formulation. As shown in Figure 6, they can contribute > 20% of the overall cost per gallon of a typical two component epoxy primer formulation. The anticorrosive pigment such as zinc phosphate makes up 15-18% by volume of the formulation.

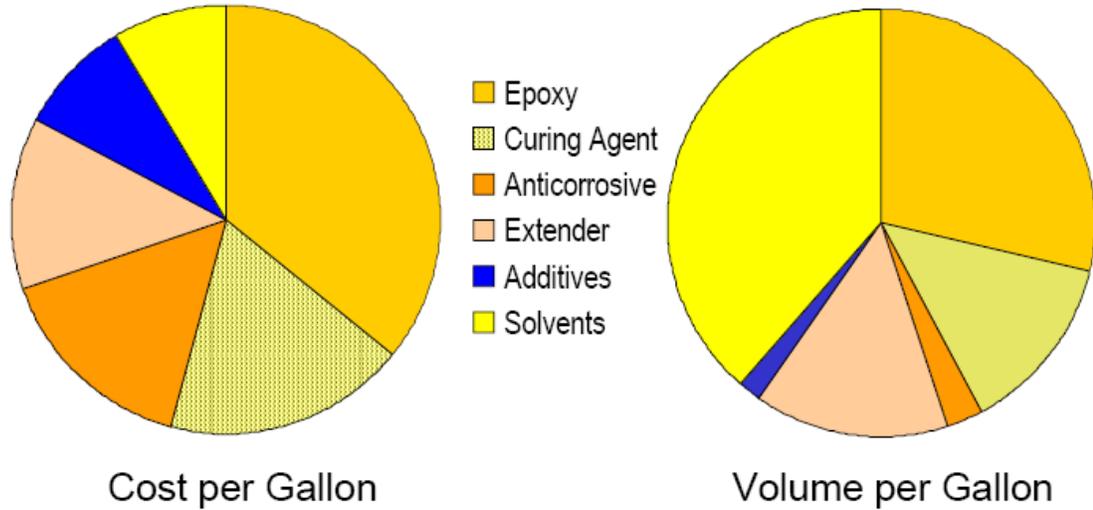


Figure 5: Cost and volume breakdown of a typical epoxy primer formulation  
(Courtesy of Air Products, Inc)

The following examples shown in figure 6-8 illustrate the effectiveness of H-300 in enhancing the long-term corrosion protection of various coatings compared to more traditional zinc phosphate type pigments. H-300 was tested against other zinc phosphates often recommended at the loading level shown in each caption. The advantage of lower cost, enhanced synergy, and increased pigment alkalinity is responsible for the improved performance over the other commercial products shown here.

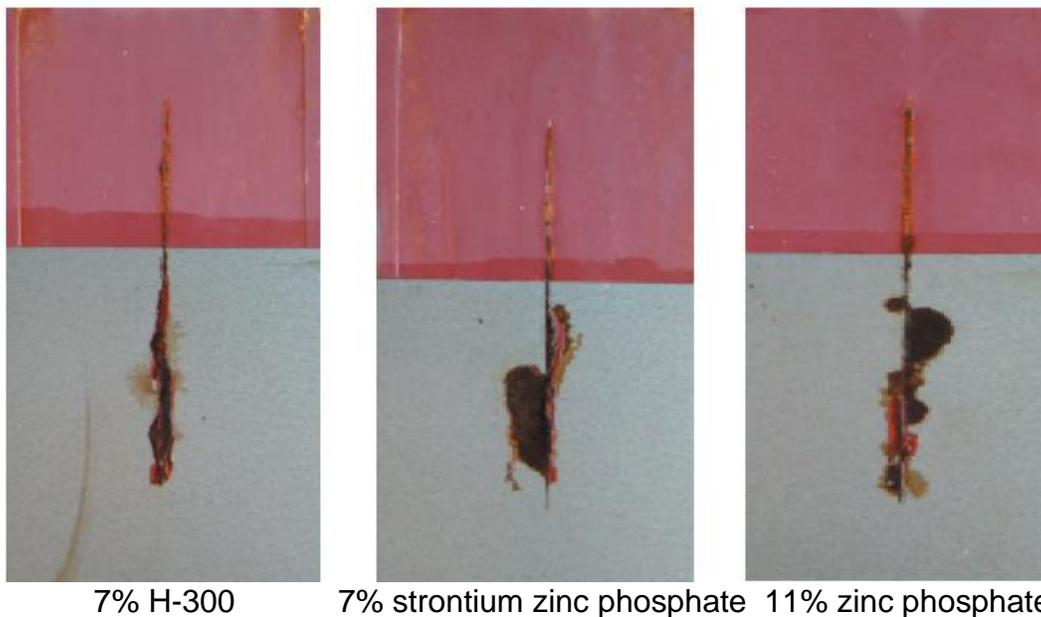


Figure 6: Comparative corrosion resistance vs. zinc phosphate inhibitive pigments in a solvent-based high solids epoxy coating after 1000 hours of salt spray (cold rolled steel)

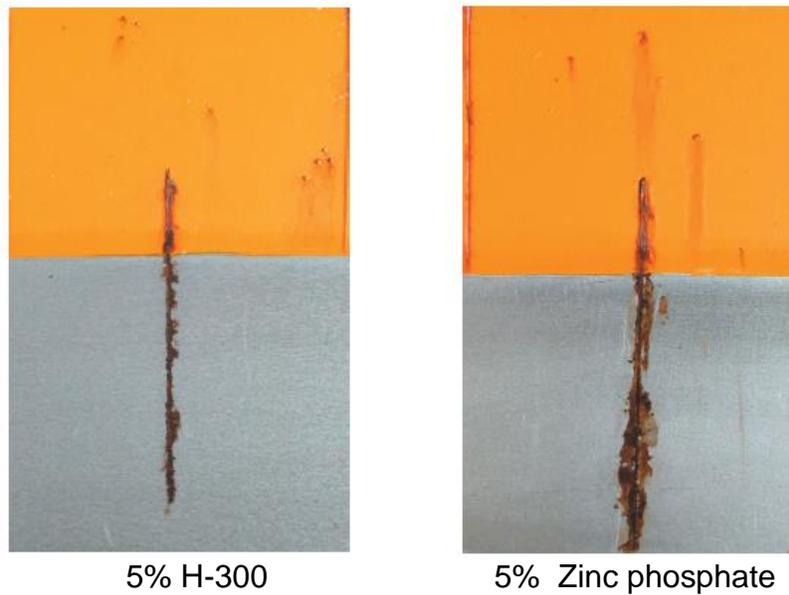


Figure 7: Comparative corrosion resistance vs. standard zinc phosphate inhibitive pigments in a water-based acrylic coating after 750 hours of salt spray (cold rolled steel)



Blank control            6% H-300            6% Mod Zinc Phosphate    6% Mod Zinc Phosphate

Figure 8: Comparative corrosion resistance vs. standard zinc phosphate inhibitive pigments in a water-based alkyd coating after 500 hours of salt spray (cold rolled steel)

## Conclusion

Ultimately, environmental concerns coupled to the rising fuel costs will drive the development of new products. Rising fuel costs lead to higher raw material costs, which implies chemists will inevitably look at reformulating paint systems currently using traditional nontoxic zinc phosphate and toxic chromate-based corrosion inhibitors. This regulation changes in the coatings market seems inevitable. It is a question of when and not if it will happen. The corrosion inhibitors described in this paper represent viable alternatives from a performance standpoint. By utilizing new inhibitive technologies and re-engineering traditional products one is able to cost effectively optimize current paint formulations with non-toxic corrosion inhibitor chemistries.

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