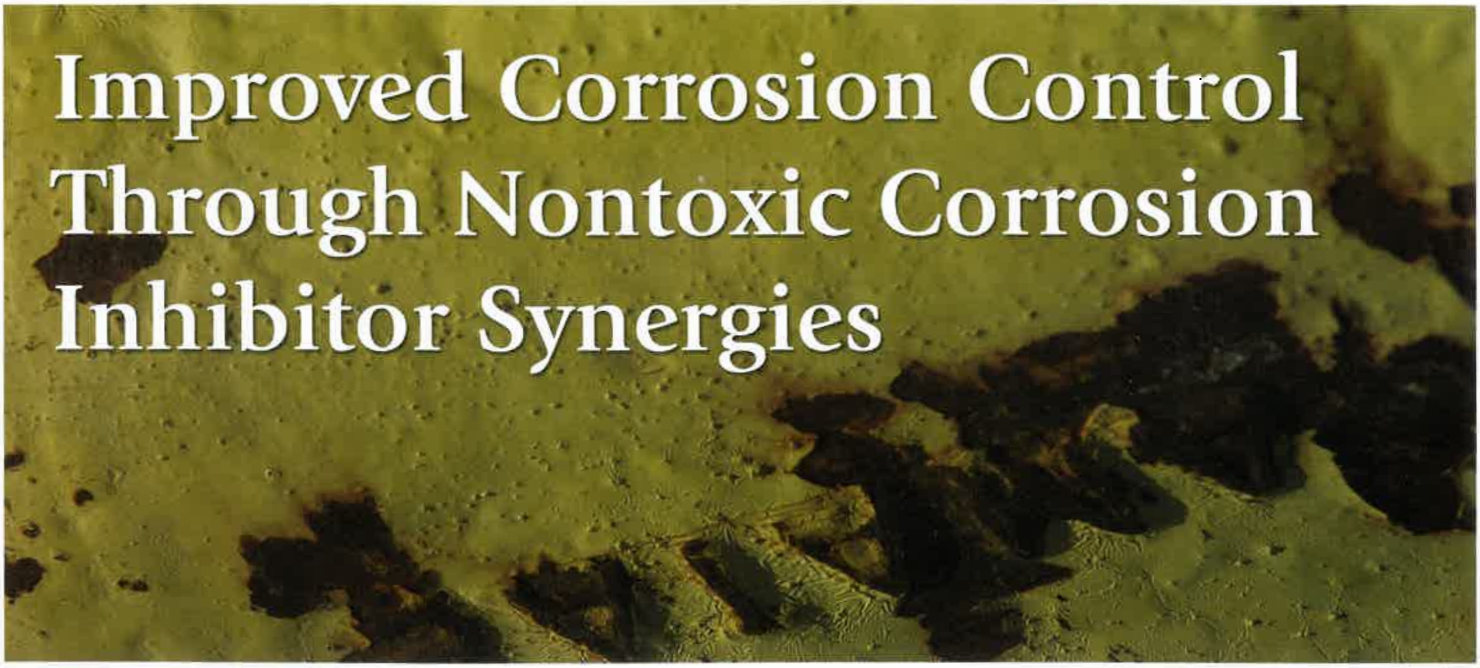
Improved Corrosion Control Through Nontoxic Corrosion Inhibitor Synergies



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The idea of anticorrosive synergies is not a new concept but one that still holds a lot of promise for advancing the performance of environmentally compliant protective coatings. The most environmentally sound method for surpassing the high anticorrosion standards set by toxic inhibitors such as lead- and chrome-base inhibitors is through the gains provided by nontoxic corrosion inhibitors synergies.

In order to realize the benefits that exist from combining inhibitor chemistries, one must first understand the mechanisms surrounding corrosion, the inhibitors themselves, and the key formulating guidelines required for success. "Solubility optimization" of the inhibitors in the coating film is an important factor for improving anticorrosive performance. Resin type and formula parameters play a significant role in inhibitor selection and use level. This synergistic approach for improving performance also carries through to other components such as extender pigments and additives. Once the synergistic balance is achieved, the results are a clear indication of the power of this theory.

INTRODUCTION

The economic cost of corrosion throughout the world is enormous. A study, jointly conducted by the Battelle Columbus Laboratories and the National Bureau of Standards (NBS) in 1975, showed corrosion to equal approximately 4.2% of the gross national product (GNP) for the United States.[1,2] A more recent study conducted in 1998, administered by Federal Highway Administration (FHWA) and performed by a team led by CC Technologies in collaboration with NACE International, showed that corrosion accounted for 3.14% of the GNP. Similar studies have also been conducted in other countries and have shown corrosion to account for anywhere from 1.5% in Australia[3] to 5.2% in Kuwait[4] of the respective countries' GNP.

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Although it is not possible to completely stop corrosion, it is possible to drastically reduce the corrosive process through the use of inhibitor-containing coatings. Coatings containing either chromates or lead-based anticorrosives have long been used to drastically reduce the corrosion rates of various metals. Performance of these toxic inhibitors has been proven time and again over a variety of substrates but, due to the toxicity associated with both, their use in coatings has diminished in the past 20 years and has been replaced, primarily by strontium, zinc, and barium (excluding $BaSO_4$) based corrosion inhibitors. Being heavy metal based, these corrosion inhibitors too have come under recent scrutiny by many health authorities throughout the world, who classify them as aquatic toxics. In fact, in some regions their use is either being very limited or phased out. Hence, the arsenal of corrosion inhibitors available to a formulator becomes smaller. However, a good understanding of the mechanisms of both "nontoxic" inorganic and organic corrosion inhibitors, as well as the possible synergies that exist between corrosion inhibitors, allows for the creation of high performance, "nontoxic" anticorrosive coatings.

CHARACTERISTICS OF NONTOXIC INORGANIC INHIBITORS

Inorganic-based corrosion inhibitors have long been used in coatings to prevent corrosion. These types of corrosion inhibitors can be divided broadly into either direct or indirect corrosion inhibitor classifications. Indirect inhibitors typically require a reaction with other raw materials in a coating to form a by-product which becomes the active corrosion inhibitor species, while a direct inhibitor is essentially active in nature and does not require a reaction. The classic example of an indirect inhibitor would be red lead, while an example of a direct inhibitor would be zinc phosphate. The focus here will be nontoxic direct, inorganic inhibitors, that function primarily through (1) anodic and/or cathodic passivation and (2) improved barrier properties.

MECHANISMS OF CORROSION PROTECTION—INORGANIC INHIBITORS

Anodic and Cathodic Passivation

Inorganic inhibitors control corrosion in neutral solutions by acting as polarizing agents to slow the three elements of the corrosion process: anodic reactions, cathodic reactions, and ionic currents in the solution and the metal itself.[5] These inhibitors increase the likelihood of a chemical reaction which result in a "passive"—protective layer on the surface of the metal. In the simplest of terms, these inhibitors act to short-circuit the electrochemical reactions that take place during corrosion.

The anodic dissolution reaction involves a release of metal ions, as well as a release of electrons. The anodic passivators discussed here refer to inhibitors that enhance chemisorption of dissolved oxygen and migrate readily to the anodic sites.[6] In turn, these inhibitors react to form salts which act as a protective barrier.

On the contrary, cathodic reactions involve a reduction of dissolved oxygen and a consumption of electrons. Cathodic passivators impede corrosion by forming surface deposits at the inactive sites within a metal. These surface deposits reduce the access of oxygen to the cathode.[7]

Improved Barrier Properties

Often overlooked as critical factors for inorganic corrosion inhibitors, the mean particle size and the overall particle morphology of an inorganic corrosion inhibitor can greatly impact the corrosion performance in a given system. Many of the commercially available inhibitors on the market contain essentially inactive "carrier" pigments which can either enhance or detract from the corrosion performance. Theoretically, any carrier pigment which impedes the migration of electrolyte to the surface would be thought beneficial, but it is often not that simple when formulating due to the dynamic nature of coatings. It is known that most nontoxic inhibitors are oxygen dependent (non-oxidizing), hence the performance of these inhibitors are both resin system-specific and pigment volume concentration (PVC) sensitive. Thus, a corrosion inhibitor that contains a carrier, which impedes an electrolyte through a coating film, might be beneficial to end corrosion performance in one resin system, while detrimental in another.

Figure 1—Mechanism of a direct, nontoxic inorganic corrosion inhibitor.

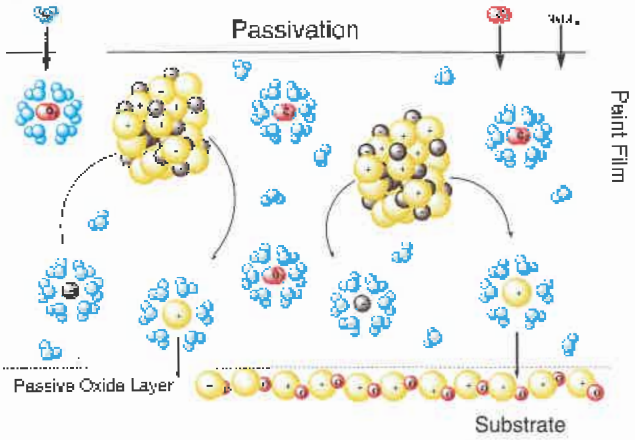


Table 1—Attributes of Organic Corrosion Inhibitors

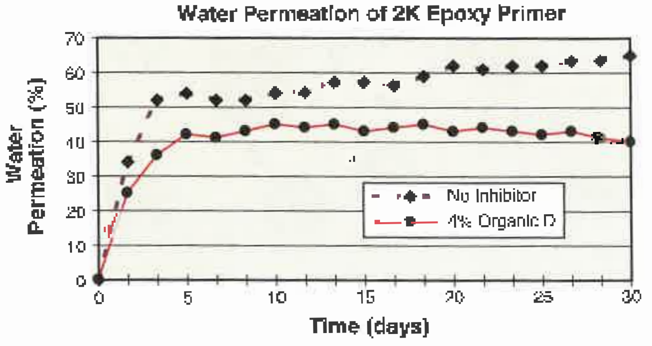
Inhibitor	Chemistry	Corrosion Protection	System Examples
Organic A	Acid amine adduct	Waterborne: • Long-term • Flash rust • In-Can rust	Water reducible alkyds, acrylic, alkyd acrylic, polyurethane, epoxy
Organic B	Organic diacid 100 % active	Solventborne: • Long-term	Coil, Powder, Wash primers, Acid-catalyzed system
Organic C	Organic diacid 60 % active	Waterborne: • Flash rust • In-Can rust	Acrylics, Polyurethane
Organic D	Organic diacid Amine adduct	Solventborne: • Long-term	Epoxy, Epoxy esters, alkyds, acrlic, polyurethane
Organic E	Polymeric amine salt solution	Waterborne: • Long-term	Epoxy, polyurethane, hybrids
Organic F	Amine carboxylate salt solution	Waterborne: • Long-term • Flash rust	Acrylic, water reducible alkyds

One trend in our industry is to reduce the film thickness of an applied coating. As the film thickness of coatings is reduced, the raw materials used in these coatings must adhere to more stringent guidelines: most notably, lower mean particle sizes. At thinner films, coatings are much less reliant on barrier properties to prevent corrosion. Formulators will typically turn to either organic inhibitors, which will be discussed later, or nanotechnologies, which is beyond the scope of this article.

CHARACTERISTICS OF ORGANIC INHIBITORS

Organic-based corrosion inhibitors allow for the creation of optimal performing thin film and high gloss corrosion resistant coatings. Organic inhibitors can: (1) enhance the barrier properties of the coating, (2) function as anodic passivators, (3) improve the adhesion of coatings, (4) aid in surface wetting, and (5) increase the performance at defect sites in the film. The organic inhibitors described herein can be classified as amine carboxylate or amine adducts of organic acid or diacid complexes. *Table* 1 compares the chemistry and corrosion protection mechanisms of the organic inhibitor compounds under discussion.

Figure 2—Decreased water uptake in a two-component epoxy primer (determined by EIS).



MECHANISMS OF CORROSION PROTECTION—ORGANIC INHIBITORS

Improved Barrier Properties

Organic corrosion inhibitors can decrease the permeability of the coating to water and corrosive ions such as sulfate and chloride. The corrosion resistance of a coating is, therefore, enhanced by decreasing the concentration of corrosive ions that reach the substrate. Electrochemical Impedance Spectroscopy (EIS) provides useful information on the water uptake by a coating. An example is shown in *Figure* 2, where significantly reduced water uptake in a two-component solventborne coating containing Organic D (an organic diacid amine adduct) is compared to a blank control with no inhibitor. A decrease in the coating's water uptake translates to increased long-term corrosion resistance of the coating.

The decrease in water permeability of the coating is attributed to (1) improved crosslinking of the paint film, (2) reduction in the coating's hydrophilic nature due to the hydrophobic interaction of the inhibitor with the polymer backbone, and (3) a decrease in the solubility of pigment additives with a high osmotic potential.

Anodic Passivation

The electrochemical technique of linear sweep voltammetry (LSV) can be used to elucidate anodic[8,9] passivation or metal-oxide film formation on corrodible substrates. The strong adsorption of organic inhibitors such as Organic A and Organic F causes the corrosion potential of the substrate to shift in the positive (anodic) direction away from the equilibrium potential of the substrate. The stronger the adsorption of the acid moiety, the greater the positive shift in the corrosion potential. This translates to a stronger anodic passivation. As shown in *Figure* 3, Organic A causes a 15–20 mV positive shift in the corrosion potential of bare steel polarized in a solution of 0.12 M $NaClO_4$. As with inhibitive pigments, organic corrosion inhibitors provide protection through an active mechanism. However, unlike inhibitive pigments, which depend on the direct dissolution of ions from the pigment, organic corrosion inhibitors directly interact with the metal surface to form a protective film. Organic A and Organic F are particularly suited as corrosion inhibitors where high gloss must be maintained. Both of these inhibitors do not negatively impact the gloss as compared to inhibitive inorganic pigments such as zinc phosphate and strontium zinc phosphosilicate (*Figure* 6).

Improved Adhesion

The adhesion improvement of Organic B, Organic D, and Organic F is attributed to their aminosilane and/or carboxylic acid functional groups, which allows them to localize between the coating and metal interface. Organic E can be distinguished from other products in that it functions as both an adhesion promoter and a corrosion inhibitor. Through hydrogen bonding of the polymer with the metal or metal oxide[10] surface, these inhibitors can act as adhesion promoters. The localization of these functional groups (COO^-, NH, Si–O–H) at the interface expels water and improves the coatings adhesion to the substrate. This adhesion improvement is particularly noticeable under high humidity conditions, or wet adhesion, which could especially benefit, for example, epoxy mastic coatings, which rely solely on barrier protection yet usually fail because of poor adhesion.

Figure 3—Degassed solution (pH 7.5, 25°C) showing a positive potential shift (red curve), effected by 0.01 M (Organic A) in 0.12 M $NaClO_4$ electrolyte.

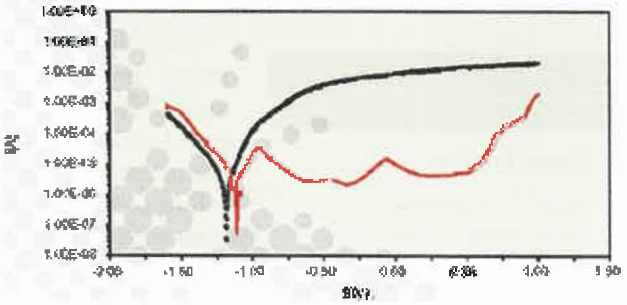
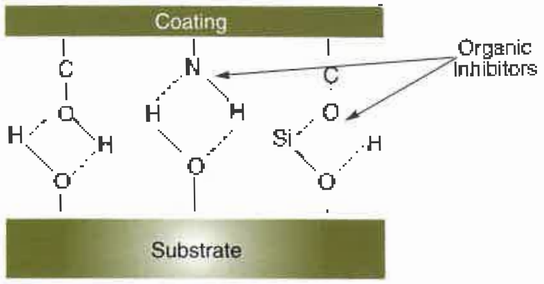


Figure 4—Adhesion promoted through multiple hydrogen bonding sites. (Organic inhibitors act as a glue between the coating and the substrate.)



Wetting

The surface wetting capability of Organic B or Organic D is attributed to the stronger attraction between molecules of these inhibitors with the molecules of the substrate than to each other. The wetting ability of these corrosion inhibitors is a function of the surface energies of the solid-gas interface, the inhibitor-gas interface, and the solid-inhibitor interface. By measuring the tangent of the contact angle between a droplet of the paint resin and a flat substrate, an assessment can be made regarding wetting. The lower the angle, the better the wetting. In a simple model system, a droplet of a 60% short oil alkyd solution in xylene was applied to steel yielding a contact angle of 114°. When 2% of Organic D was added, the angle dropped to 78°, indicating significantly improved wetting.

Decreased Coating Imperfections

Coating imperfections are ubiquitous and occur randomly in paint films. Such pores or imperfections cause ingress of electrolyte into the film, which promotes localized corrosion. Where defects occur, local-

Figure 5—Contact angle measured between a drop of resin solution without inhibitor (left) and with 2% Organic D (right).

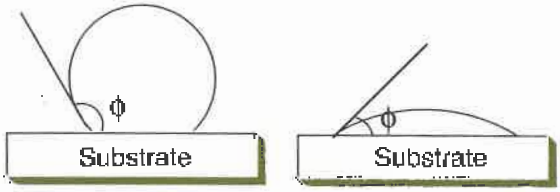


Figure 6—Organic A, Organic E, and Organic F can combine with Fe-ions to form insoluble complexes (left) to plug anodic defect sites (right).

ized galvanic cells are created and Fe-ions are released. These ions combine with organic corrosion inhibitors such as Organic A, Organic B, Organic E, and Organic F to form insoluble complexes at the defect site, which literally plug the defect, thus disrupting the galvanic cell established and thus reducing corrosion.

ORGANIC INHIBITOR—FORMULATION GUIDELINES FOR CHEMISTS

The following guidelines underscore the importance of understanding the compatibility and incorporation techniques needed to avoid difficulties, such as viscosity changes, in order to achieve optimum performance. In most cases, the organic inhibitors should be added to the amine portion of two-component epoxies, or the polyol portion of a two-component polyurethane system. When the organic compound is a solid, it *should* be added to the grind phase, and when it is a liquid, it *may* be added (during the let-down phase for example). Use levels are typically between 2–4% based on total formulation solids, although lower levels may be used for flash rust inhibition. A ladder of concentrations is recommended to determine optimum levels.

Since Organic B has free carboxylic acids, it is better suited to resin systems such as those used in coil and powder coatings, e.g., polyester-melamine TGIC, or wash primers based on polyvinyl butyral. The "blocked" version of Organic B with an alkyl amine is Organic D, and is suited for solventborne systems.

Organic A and Organic F are especially suitable for waterborne coating systems. Organic F can be used as is without need for further pre-neutralization. Organic F provides flash rust protection especially on weld seams and long-term corrosion protection in waterborne coating systems. Organic A should be pre-neutralized to a pH between 8 and 9 prior to incorporation using a low molecular weight amine. The amine should have sufficient volatility to leave the coating during the curing conditions. In this way, Organic A provides effective in-can and flash rust corrosion protection while the paint is wet, but a water insoluble complex is re-formed when the coating cures, and Organic A acid then provides long-term corrosion protection. This is a significant advantage over other flash rust inhibitors (e.g., sodium nitrite), which have no direct influence on long-term protection, except, perhaps, a possible adverse effect because they remain in the paint and are water-soluble. A special grade of Organic B supplied as a flake cake in water is Organic C. Organic C should be pre-neutralized in the same way as Organic A.

Organic/Inhibitor Synergy Example

Figure 7 features some examples under particularly tough exposure conditions where an organic/inorganic blend of corrosion inhibitors show performance at least comparable to commercial alternatives.

Coil coating applications are headed toward chromate-free universal primers due to the harmful effects of Cr (VI) found in zinc and strontium chromate corrosion inhibitors. As shown in *Figure* 7, the nontoxic alternative to strontium chromate consisting of a calcium-based ion exchange inhibitive pigment and an organic diacid (Organic B) improves the coatings corrosion resistance along the cut-edge (bottom of panel) and at the scribe. Coil coaters are switching away from chromate conversion coatings (CCC) due to the high cost associated with disposal of chromate conversion solutions.

Table 2—Attributes of Hybrid A: A New Zinc-Free Anticorrosive Pigment

Inhibitor	**Chemistry**	**Corrosion Protection**	**System Examples**
Hybrid A	Anodic Passivation/ Ion Scavenging-Exchange	Waterborne: • Long-term Solventborne: • Long-term	Acrylics, polyurethane, alkyds, epoxy, hybrids (Acrylic epoxy, acrylic Alkyds), Water- Reducible Alkyds

Currently, hexavalent chromium is used in two key areas of coil coating: pretreatments and primers. Because it possesses unique corrosion-inhibiting properties on a variety of metallic substrates, it is not at all clear where—or even if—its usage can be eliminated or substantially reduced in the North American marketplace. Both the pretreatment manufacturers and the coatings community have been hard at work on "chrome free" systems for the better part of 20 years, but with only mixed results. One of the serendipitous properties of chromate inhibitive pigments is that they tend to work over multiple substrates, but this has not proven true with either the so-called "white pigments" which are being proposed to replace hexavalent chromium pigments in chrome-free primers, or with the nonchromate chemistries which are being explored in "chrome-free" pretreatments. There has been a certain amount of success in the aluminum arena; both chrome-free pretreatments and primers are commercially available from multiple sources, and are being used on a daily basis. Their quality seems to be acceptable, although it is not clear if the new chrome-free systems fully address the concerns surrounding filiform corrosion.[11]

NEW GENERATION OF ZINC-FREE INORGANIC CORROSION INHIBITORS

There is a new breed of inhibitor on the market we shall refer to here as Hybrid A. Hybrid A represents a new generation of environmentally friendly, inorganic zinc-free corrosion inhibitor based on anodic passivation and a unique selective ion scavenging and exchange mechanism. 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 200,000 kg/year or releases to water exceed 100,000 kg/year. Zinc can significantly affect local aquatic environments, accumulating in aquatic organisms (but not plants) and poisoning species that then eat them.[12]

Hybrid A was developed to fulfill the need for an effective corrosion inhibitor for waterborne and solventborne coatings that could perform equal to or better than any zinc-based inhibitive pigment. Hybrid A leaves no environmental footprint and is based on constituent components that are Generally Recognized as Safe (GRAS) for food by the Food & Drug Administration.[13]

Unique Characteristics of Hybrid A

Hybrid A combines the unique synergistic properties of anodic 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

Figure 7– Organic B with an inorganic corrosion inhibitor in a coil coating application.

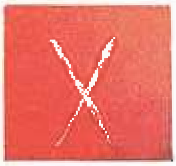
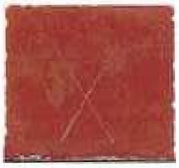
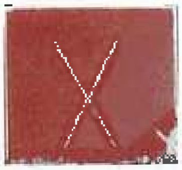
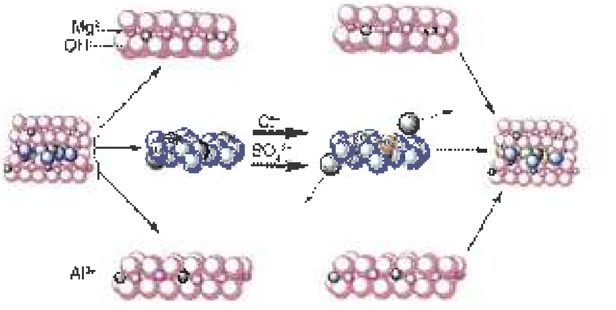
After 400h Salt Spray Test **ASTM B 117-90**	**Without Inhibitor**	**Commercial System ($SrCrO_4$)**	**4% Organic B +1 8.5% Ca-ion Exchanged Pigment**
Substrate: Hot dip galvanized steel			
Primer: TPA, phenolic resin, phosphoric acid pre-treatment			
Topcoat: PES melamine			
Delamination at scribe (mm)	5	2	1
Under cutting at scribe (mm)	0	0	0
After 1500h Salt Spray Test **ASTM B 117-90**	**Without Inhibitor**	**Commercial System (X% $SrCrO_4$)**	**4% Organic B + 18.5% Ca-ion Exchanged Pigment**
Substrate: Al/Zn steel			
Primer: TPA, phenolic resin, phosphoric acid pre-treatment			
Topcoat: PVC Plastisol			
Delamination at scribe (mm)	Total	0	0
Delamination at cut edge (mm)	Total	0	1.5
Under cutting at scribe (mm)	0	0	0
Under cutting at cut edge (mm)	3	1	1.5

Figure 8—Ion scavenging and exchange mechanism of Hybrid A showing the trapping of chloride and sulfate ions in the lattice structure.

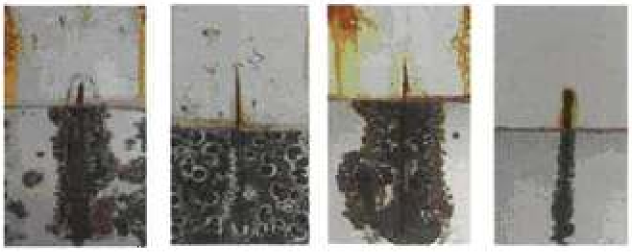


their corrosion ions (typically phosphate or silicate) in order to impart corrosion resistance to coatings. Hybrid A is an effective corrosive ion scavenger as well as an anodic passivator. The product does not contain any heavy metals. Instead, it relies on its high porosity to scavenge and adsorb chloride and sulfate ions, thus decreasing their ability to cause corrosion at the substrate. The anodic 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 (e.g., calcium) from a high surface area amorphous silica carrier. Hybrid A does not contain silica.

Figure 8 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 and releasing inhibitive 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 9 shows the effectiveness of the new generation Hybrid A in enhancing the long-term corrosion protection of a water-based coating with primer and topcoat.

Figure 9—Comparison of corrosion resistance of zinc-free inhibitive pigments in a water-based acrylic coating after 336 hr of salt spray (ASTM B-117).



Blank Control | 7% Zinc-Free Competitor A | 7% Zinc-Free Competitor B | 5% Hybrid A

CONCLUSION

The protection of workers and the environment will continue to be the driving force toward optimizing paint systems currently using lead and chromate-based corrosion inhibitors. This regulatory change seems inevitable; it is not a matter of "if" but of "when." The corrosion inhibitors described in this article represent viable alternatives from a corrosion performance point of view. By blending the chemistries described here, one is able to cost effectively optimize their formulation with nontoxic corrosion inhibitor chemistries. Aware of the power of inhibitor synergies, corrosion inhibitor manufacturers are now tailoring their inhibitors to meet the ever-changing performance and environmental demands of our industry. One such example presented here is the Hybrid A corrosion inhibitor, a new generation of nontoxic heavy metal-free inhibitive pigment. CT

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