

ECOFRIENDLY CORROSION INHIBITING ADDITIVES FOR TOMORROWS COATINGS

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Abstract

Until recently, heavy metal-based corrosion inhibitors were widely accepted as the only materials that could provide the corrosion protection needed in Paints & Coatings. Corrosion inhibitors provide an indispensable function to protective coatings. The performance of a coating under corrosive conditions requires that corrosion inhibitors provide sustainable protection during the coatings warranty. The coating industry, however, is challenged to be more cognizant of the impact toxic metals have on human health and the environment. In response to the European Directive 1999/45/EC Advancement of Technical Progress (ATP) amendment 29 effective October 2005, products containing zinc oxide and zinc phosphate required hazardous labeling due to their marine toxicity. The growing pressure to replace zinc, barium, strontium, and other heavy metals has shifted the coatings pendulum to more eco-friendly alternatives. This paper captures specific products reflecting the new paradigm of technologies based on heavy-metal free inorganic pigments as well as non-toxic organic corrosion inhibitors.

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 3.1% 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 countries' GNP. 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 anti-corrosives 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 twenty years and has been replaced primarily by zinc, molybdenum, strontium, and barium based corrosion inhibitors. Being heavy metal based, these corrosion inhibitors too have come under recent scrutiny by many health authorities throughout the world, deeming them as aquatic toxins, and in fact, in some regions their use is either being limited or phased out. As a result, the arsenal of corrosion inhibitors available to a paint formulator has begun to shrink. A good understanding of the mechanisms of both non-toxic inorganic and organic corrosion inhibitors, as well as the possible synergies that

exist between corrosion inhibitors, allows for the creation of high performance, non-toxic anti-corrosive coatings.

Non-Toxic Inorganic Corrosion Inhibitors

Inorganic-based corrosion inhibitors have long been used in coatings to prevent corrosion. These types of corrosion inhibitors can broadly be divided into either direct or indirect corrosion inhibitor classifications. Indirect inhibitors typically require a reaction with other raw materials in a coating (e.g. acidic groups) 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 secondary reaction. The classic example of an indirect inhibitor would be red lead (Pb_3O_4), while an example of a direct inhibitor would be Zinc phosphate. The focus of this paper will be on non-toxic, direct inorganic inhibitors, which function primarily through (1) anodic and/or cathodic passivation and (2) improved barrier properties.

Inorganic Corrosion Inhibitors: How do they work?

A) 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 will result in a “passive” – protective layer on the surface of the metal. In simple terms, these inhibitors act to short-circuit the electrochemical reactions, which take place during corrosion. The anodic dissolution reaction involves a release of metal ions into solution, as well as a generation of electrons at the cathode. The anodic passivators discussed here depend on 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 passivators impede corrosion by forming surface deposits (precipitates) at the inactive sites within a metal. These surface deposits reduce the access of oxygen to the cathode (7).

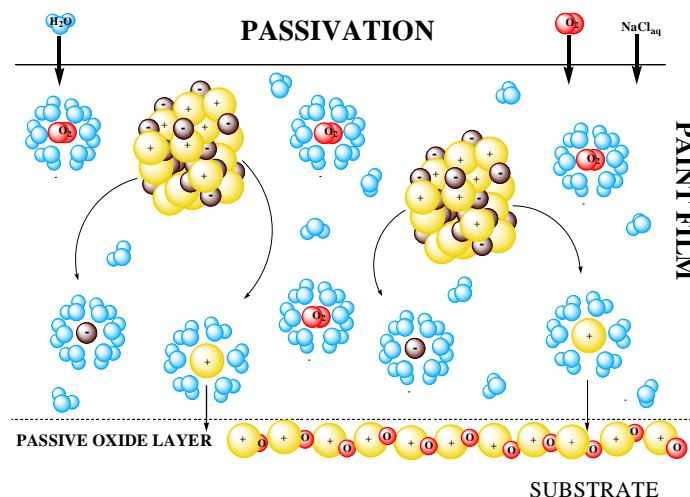


Figure 1: Schematic mechanism of a direct, non-toxic inorganic corrosion inhibitor.

B) Improved Barrier Properties

Although they are two of the most critical factors often overlooked in inorganic corrosion inhibitors, the mean particle size and the overall particle morphology 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 enhance or detract from the overall corrosion performance. Theoretically, any pigment which by means of its shape or morphology impedes migration of electrolyte to the metal surface would be considered beneficial. However, it is often not as simple as choosing the right shaped pigment or particle size when formulating protective coatings due to the dynamic nature of coatings and the interaction of multiple additives in the paint. It is known that most non-toxic inhibitors are oxygen dependent (i.e., non-oxidizing), hence the performance of these inhibitors is both resin system specific and pigment volume concentration (PVC) dependent. Thus, a corrosion inhibitor over an inert carrier, which impedes an electrolyte through a coating film, might be beneficial in one resin system, while detrimental in another. One economic trend in our industry is to reduce the film thickness of the applied coating to save costs or reduce labor. As the film thickness of coatings is reduced, the raw materials used in these coatings must adhere to more stringent requirements, most notably, lower mean particle size, decreased oil absorption, and better dispersion. At reduced film thickness, coatings are less reliant on barrier properties to prevent corrosion. Formulators will typically turn to either organic inhibitors, which will be discussed later in this paper, or novel nanotechnologies, which is beyond the scope of this paper.

New Generation of Zinc-Free Inorganic Corrosion Inhibitors

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. (12) 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 (13).

Unique Characteristics of Hybrid A

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"> • Long-term Solvent-borne <ul style="list-style-type: none"> • Long-term 	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.

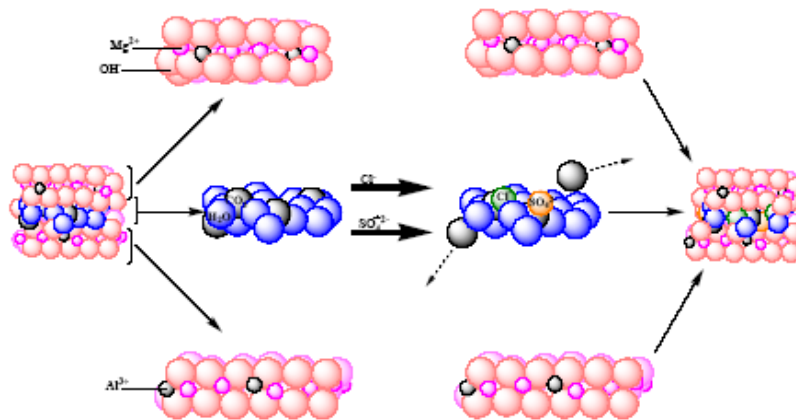


Figure 2: Ion scavenging & exchange mechanism of Hybrid A showing the trapping of chloride and sulfate ions in the host lattice structure

The example shown in figure 3 illustrates the effectiveness of Hybrid A in enhancing the long-term corrosion protection of an acrylic water-based coating with primer and topcoat. 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 systems 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.

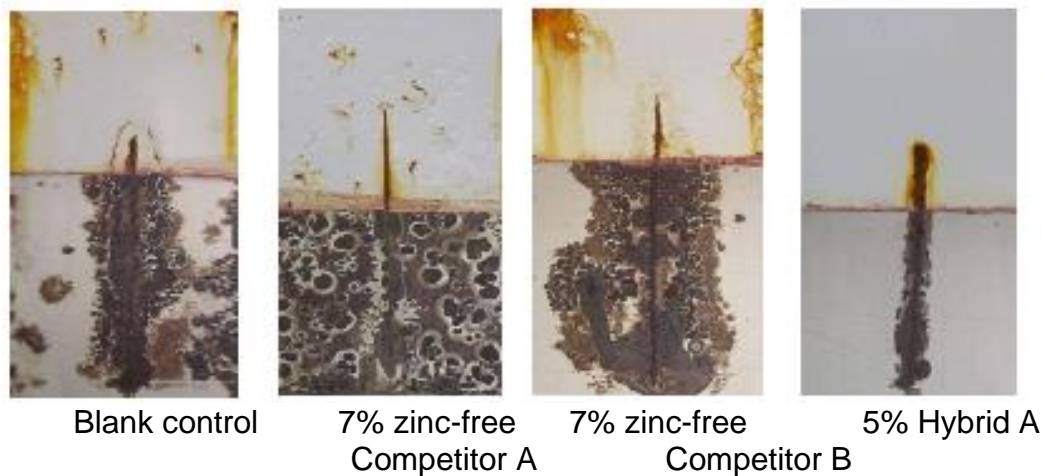


Figure 3: Comparative corrosion resistance of zinc-free inhibitive pigments in a water-based acrylic coating after 336 hours of salt spray

Organic Inhibitors: Another alternative to heavy metal corrosion inhibitors

An alternative approach to eliminating heavy metal and toxic materials is through use of organic corrosion inhibitors. Organic-based corrosion inhibitors allow for the creation of 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 2 compares the chemistry and corrosion protection mechanisms of the organic inhibitor compounds under discussion.

Table 2: Attributes of Organic Corrosion Inhibitors

Inhibitor	Chemistry	Corrosion Protection	System examples
Organic A	Acid Amine Adduct	Waterborne: <ul style="list-style-type: none"> • Long-term • Flash Rust • In Can Rust 	Water Reducible Alkyds, Acrylic, Alkyd acrylic, Polyurethane, Epoxy

Organic B	Organic Diacid 100 % active	Solvent-borne <ul style="list-style-type: none"> • Long-term 	Coil, Powder, Wash Primers, Acid catalyzed systems (See figure 9)
Organic C	Organic Diacid 60 % active (filter cake)	Waterborne <ul style="list-style-type: none"> • Flash Rust • In Can Rust 	Acrylics, Polyurethane
Organic D	Organic Diacid Amine Adduct	Solvent-borne <ul style="list-style-type: none"> • Long-term 	Epoxy, Epoxy Esters, Alkyds, Acrylic, Polyurethane
Organic E	Polymeric Amine Salt Solution	Waterborne <ul style="list-style-type: none"> • Long-term 	Epoxy, Polyurethane, Hybrids
Organic F	Amine Carboxylate Salt Solution	Waterborne <ul style="list-style-type: none"> • Long-term • Flash Rust 	Acrylic, Water Reducible Alkyds

Organic Inhibitors: How do they work?

A) 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 Fig. 4 where significantly reduced water uptake in a two-component solvent-borne coating containing Organic D (an organic Diacid Amine Adduct) compared to a blank control with no inhibitor. A decrease in the coatings water uptake translates to increased long-term corrosion resistance of the coating.

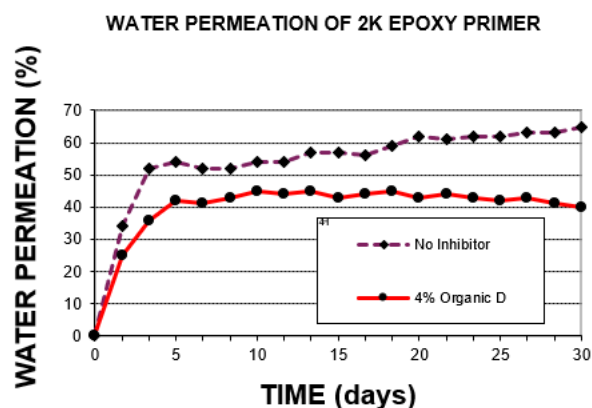


Figure 4: Decreased water uptake in a two component epoxy primer
(As determined by electrochemical impedance spectroscopy)

The decrease in water permeability of the coating is attributed to (1) improved cross-linking of the paint film (2) reduction in the coatings 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.

B) 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 5, Organic A causes a 15-20 mV positive shift in the corrosion potential of bare steel polarized in a solution of 0.12 M NaClO₄. As with inhibitive pigments, organic corrosion inhibitors provide protection through an active mechanism. But 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 these inhibitors do not negatively impact the gloss as compared to inhibitive inorganic pigments such as zinc phosphate and strontium zinc phosphosilicate.

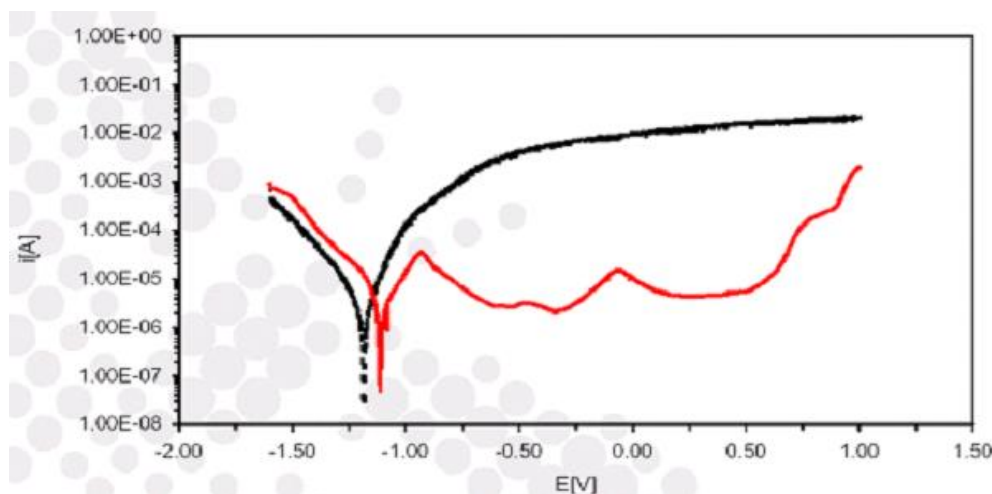


Figure 5: Degassed solution (pH 7.5, 25°C) showing a positive potential shift (red curve), effected by 0.01 M (Organic A) in 0.12 M NaClO₄ electrolyte

C) 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 (figure 6) 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.

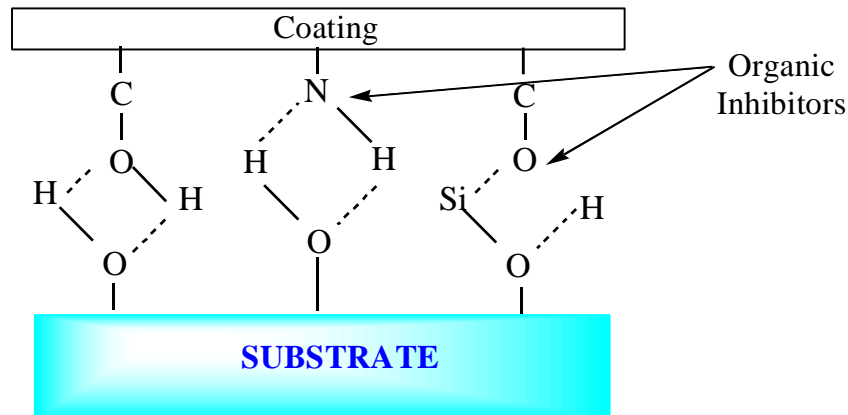


Figure 6: Adhesion promoted through multiple hydrogen bonding sites. Organic inhibitors act as a glue between the coating and the substrate

D) 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 contact 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 (Figure 7).

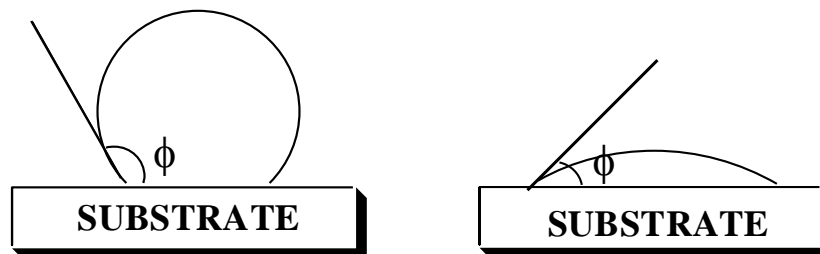


Figure 7: Contact angle measured between a drop of resin solution without inhibitor (left) and with 2% Organic D (right).

E) 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, localized 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 thus reducing corrosion.

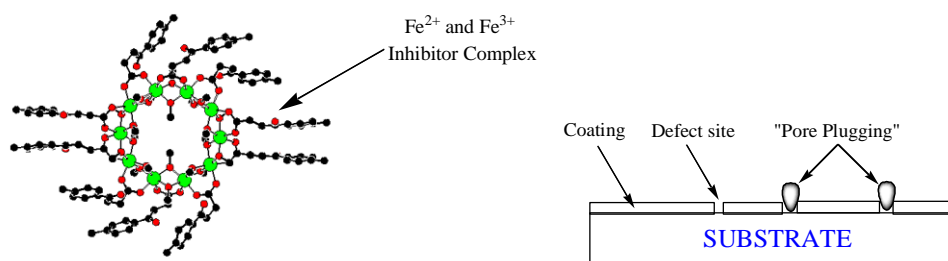


Figure 8: Organic A, Organic E, and Organic F can combine with Fe ions to form insoluble complexes (left) to plug anodic defect sites (right).

Organic Corrosion Inhibitors – Some Formulating Tips

The following guidelines emphasize importance of understanding the compatibility and incorporation techniques needed to avoid difficulties such as viscosity changes, in order to achieve optimum performance when using organic corrosion inhibitors. In most cases, the organic inhibitors should be added to the amine portion of a two-component epoxy, 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 to 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 resins systems such as those used in coil and powder coatings, e.g. polyester-melamine triglycidyl isocyanate (TGIC), or wash primers based on polyvinyl butyral (PVB). The “blocked” version of Organic B with an alkyl amine is Organic D, and is suited for solvent-borne 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, the 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 the 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 an 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. The Organic C should be pre-neutralized in the same way as the Organic A.

Inorganic-Organic Corrosion Inhibitor Synergy

Below is an example in which an organic/inorganic blend of corrosion inhibitors shows performance at least comparable to a traditional toxic heavy metal-based product.




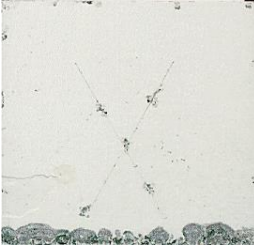
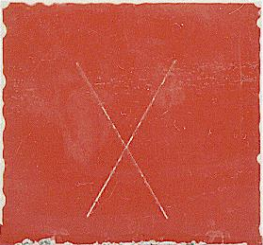

After 400h salt spray test ASTM B 117-90	Without Inhibitor	Commercial system (SrCrO ₄)	4% Organic B + 18.5% Ca-ion exchanged pigment
<u>Substrate:</u> hot dip galvanized steel <u>Primer:</u> TPA, Phenolic resin, phosphoric acid pre-treatment <u>Topcoat:</u> PES Melamine			
Delamination at scribe (mm)	5	2	1
Under cutting at scribe (mm)	0	0	0
After 1500h Salt Spray Test ASTM B 117-90	Without inhibitor	Commercial system (SrCrO ₄)	4% Organic B + 18.5% Ca-ion exchanged pigment
<u>Substrate:</u> Al/Zn steel <u>Primer:</u> TPA, phenolic resin, phosphoric acid pre-treatment <u>Topcoat:</u> 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 9: Organic B with an inorganic corrosion inhibitor in a coil coating application

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 9, the non-toxic 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 use of chromate conversion coatings (CCC) due to the high cost associated with disposal of chromate conversion solutions. 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 twenty years, but only with 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 non-chromate 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).

Conclusion

Ultimately, 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 "when". The corrosion inhibitors described in this paper represent viable alternatives from a corrosion performance point of view. By blending the chemistries described in this paper one is able to cost effectively optimize their formulation with non-toxic corrosion inhibitor chemistries. Aware of the power of inhibitor synergisms, corrosion inhibitor manufacturers are now tailoring their inhibitors to meet the constantly changing performance and environmental demands of our industry. One such example presented here is the Hybrid A corrosion inhibitor, a new generation of non-toxic heavy metal free inhibitive pigment.

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