

Water-Based Coatings Powered by Nanoparticle Vapor Corrosion Inhibitors

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Today's waterborne coatings are steadily fulfilling several requirements that are usually met by solvent-borne systems, such as good adhesion, corrosion resistance, and improved weathering. Aqueous technologies are generally preferred over their solvent-based counterparts due to ease of application, lower volatile organic compounds, and cost. However, waterborne coatings still have limitations in providing long-term protection for metals in extremely corrosive environments. Through research it

has been found that combining nanoparticle vapor phase corrosion inhibitors (NANO-VCI) with a non-zinc environmentally friendly metal complex inhibitor will significantly improve the long-term corrosion protection of acrylic paints on steel substrates. This article investigates the use of NANO-VCI technology with a non-zinc environmentally friendly metal complex inhibitor to greatly improve the long-term corrosion protection of an acrylic coating applied direct to metal.

New international environmental regulations have led to a global trend in developing coatings that are environmentally friendly. Some of these eco-friendly coatings contain only nontoxic, non-reportable raw materials that are safe to humans and/or the environment.

In this study, it has been found that the use of a nontoxic inorganic corrosion pigment combined with nanoparticle vapor phase corrosion inhibitor (NANO-VpCI[†] [VCI]) technology in a waterborne acrylic protective direct-to-metal (DTM) coating produced a synergistic anti-corrosion effect compared to using these inhibitors separately.

Corrosion inhibitors work by two primary methods. They can either absorb or coat a metal surface, protecting it from corrosive environments, or they may react chemically with a metallic element to form a non-reactive

[†]Trade name.

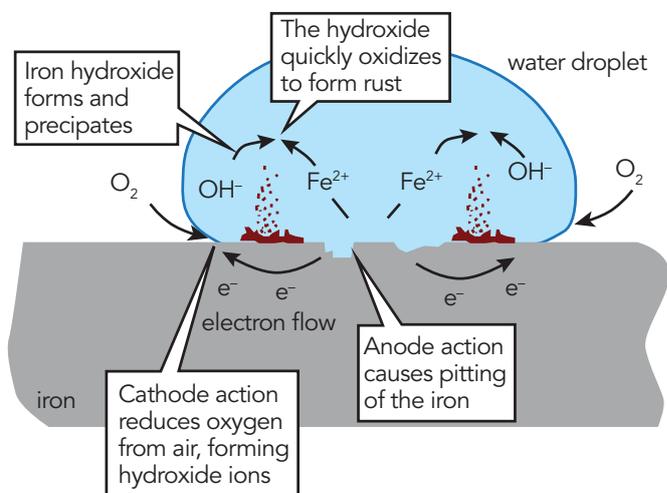
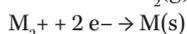
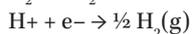
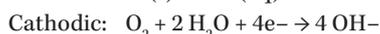
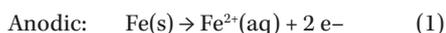


FIGURE 1. Electrochemical cell action driven by the energy of oxidation continues the corrosion process.

tive, hydrophobic (passive) layer that prevents the mechanism of corrosion to the metal substrate. To be effective, an inhibitor should interact with the anodic or cathodic sites (retarding the oxidation and reduction corrosion reactions) along with shielding water from the metal surface and preventing it and other corrosive electrolytes from coming in contact with the bare metal.

Oxidation Reaction of Iron

For steel to corrode, oxygen and water must be in direct molecular contact with the surface of the substrate (Figure 1). The anodic and cathodic reactions are shown in Equation (1):



For this experiment, a nontoxic metal-inhibiting pigment was used to provide passivation and ion scavenging protection. The inhibitor works through hydrolysis by dissociating and reacting with Fe^{2+} and OH^- ions to form $\text{Fe}(\text{PO}_4)_x$ and $\text{X}(\text{OH})_x$; both molecules then precipitate to build a passive micro-phobic layer on the metal surface. The inhibiting pigment also acts as an ion scavenger, neutralizing corrosive species such as Cl^- and SO_4^{2-} , limiting their aggressive behavior toward metal corrosion (Figure 2).

However, although a good level of corrosion protection can be obtained with this one inhibitor, it is not perfect and due to its large particle size, gaps and voids exist between the pigment particles that are entry points for micro-corrosion that can expand and lead to coating failure (Figure 3).

To improve the corrosion performance of the coating, NANO-VCI were added to the matrix. The blend of vapor phase corrosion inhibitors possesses the ability to penetrate and adhere to the metal surface under the gaps and micro-cavities providing a molecular layer of corrosion protection (Figures 4 and 5).

The mechanism of the NANO-VCI involves two parts; the first is the transport of the inhibitor to the metal surface and the

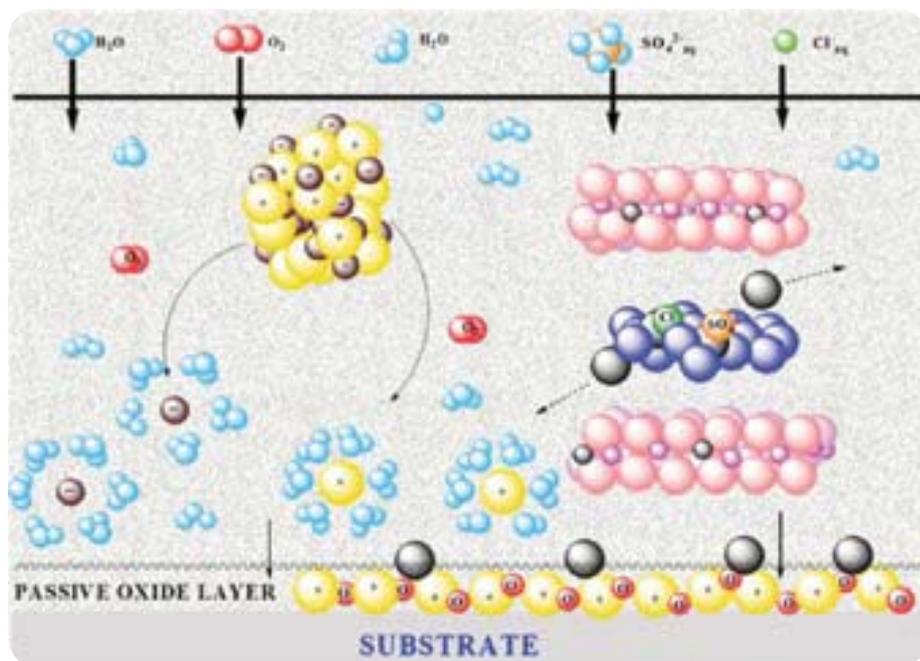


FIGURE 2. The reactions of an inhibiting pigment to provide passivation and ion scavenging protection.

second is how the inhibitor interacts on the metal substrate to form a film. When added to a liquid coating, the inhibitors in this study react with water and dissociate. After application, as the liquid coating cures, the charged inhibitors migrate and absorb onto the bare metal surface; adsorption occurs as a result of electrostatic forces between the electric charge on the metal and the ionic charges on the inhibitor molecules. Once attached to the metal, the tails of the inhibiting molecules produce a highly hydrophobic film that repels water and other corrosive species, which in turn reduces corrosion; these non-reactive films can be absorbed onto passivating layers as well (Figure 6).

At higher concentrations, NANO-VCI can also have a self-healing effect. If a fracture was to occur in a cured coating, the attractive forces of the inhibitor toward the exposed metal would cause them to migrate through the coating to the bare metal surface where they would then form a protective film. This technology is being used mostly in temporary coatings due to their softer films and low abrasion resistance.

The combination of the NANO-VCI with a nontoxic metal complex inhibitor pro-

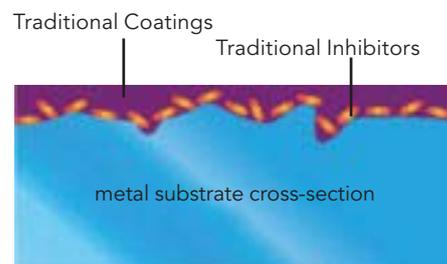


FIGURE 3. The large particle size of a traditional inhibitor can lead to micro-corrosion and eventual coating failure.

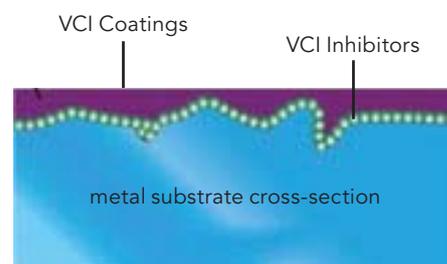


FIGURE 4. Metal substrate cross-section with VCI coatings and VCI inhibitors.



FIGURE 5. The blend of VCIs provides a molecular layer of corrosion protection.

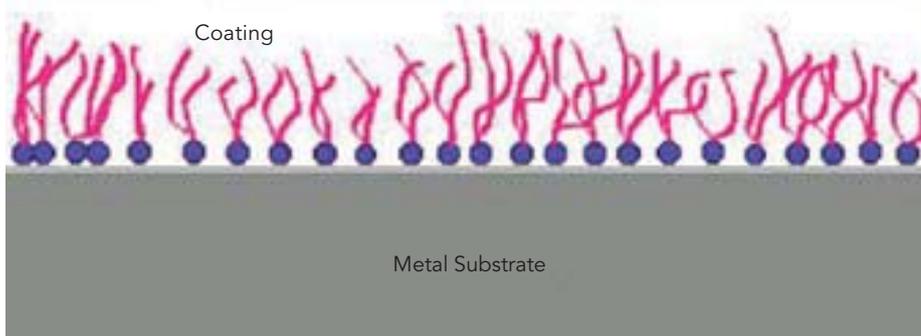


FIGURE 6. Tails of the inhibiting molecules produce a film that repels water.



FIGURE 7. Control sample, 540 h of continuous salt spray.



FIGURE 8. Close-up of Figure 7.

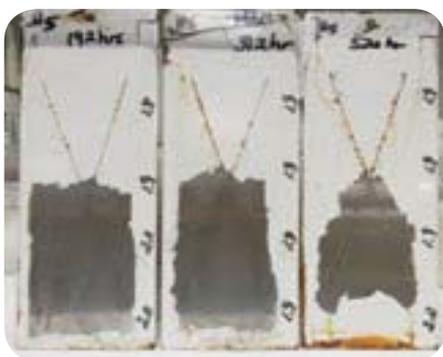


FIGURE 9. Sample containing ecologically friendly pigment inhibitor.

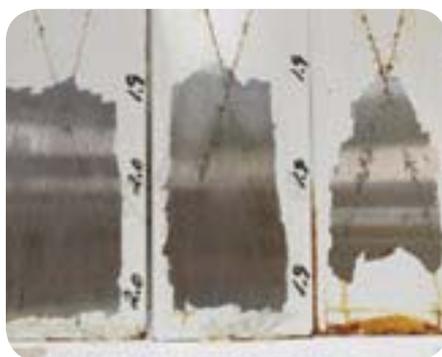


FIGURE 10. Close-up of Figure 9.



FIGURE 11. Sample containing NANO-VCI and ecologically friendly pigment inhibitor.



FIGURE 12. Close-up of Figure 11.

duced a great improvement in corrosion resistance from the synergy between the two through passivation, ion scavenging, and protective film formation.

Experimental Procedure

This study examines three self-cross-linking acrylic latex coating samples with and without the corrosion inhibitors. All samples were made using a high-speed mixer with a cowles blade.

Each coating sample was then applied to three separate CRS SAE 1010 (4 by 12-in [102 by 305-mm]) panels using a wire wound drawdown rod to produce ~2.0 mils of dry film thickness. The carbon steel specimens were prepared in accordance with ASTM B117¹ salt spray testing method.

After reaching full cure (seven days at ambient temperature), the panels were scribed as explained in method ASTM D1654.² All backs and edges of the panels were taped to prevent corrosion creep. They were then placed into a 5% sodium chloride (NaCl) salt fog chamber for environmental testing for up to 520 h. After 520 h, each sample was rinsed, scraped, and rated for creep (ASTM D1654), blistering (ASTM D714³), and degree of rusting (ASTM D610⁴). Photos were taken after testing.

Results

The main goal of the experiment was to improve the corrosion resistance of a coating through the synergy between the combination of NANO-VCI with an eco-friendly inhibiting pigment. Normally this type of long-term corrosion prevention is done by using inhibitors that are toxic and dangerous such as lead, zinc, and chromates. However, good long-term performance was achieved from the synergy of the two inhibitors mentioned in this study.

The result in Figure 7 presents the poor performance of an acrylic water-based paint with no inhibitors other than for flash rust. The paint failed ≤192 h in the salt chamber (failure ≥ 3-mm creep from scribe). The salt vapors were able to quickly penetrate the film's barrier, which leads to blistering and loss of adhesion and causing the underlying

substrate to corrode (Figure 8).

The results in Figure 9 show the coating made using only the nontoxic metal complex inhibitor. As can be seen, the overall corrosion resistance was greatly improved. The film displays a much lower level of red rust on its surface, with just a slight level of blistering near the scribes; the effectiveness of the pigment in improving passivation and ion-scavenging is clearly demonstrated. However, even though the addition of the inhibitor improved the overall corrosion resistance, the coating failed ≤ 520 h in the salt spray chamber (Figure 10).

Figure 11 shows the results for the sample containing both the NANO-VCI and ecologically friendly pigment inhibitor that passed 520 h. The addition of the VpCI clearly complemented the corrosion resistance of the coating by reducing the level of blistering and substrate corrosion that was seen with just the metal complex inhibitor alone. This again was done by the ability of the VCI to migrate underneath the microgaps and voids that exist between the pigment particles and attach itself to the metal substrate to form a protective passivating film; there is an obvious synergy between the two inhibitors (Figure 12).

Conclusions

Today's waterborne coatings are steadily fulfilling several requirements that are usually met by solvent-borne systems, making aqueous technologies preferred over their solvent-based counterparts for environmental regulation and safety reasons.

Through research it has been found that combining NANO-VCI's with a nontoxic metal complex inhibitor will significantly improve the long-term corrosion protection of acrylic paints that are applied directly to metal. The combination of these inhibitors provides a synergetic multi-layer defense of corrosion resistance through passivation, ion-scavenging, and film formation.

References

1. ASTM B117, "Salt Fog Testing" (West Conshohocken, PA: ASTM).
2. ASTM D1654, "Standard Test Method for

Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments" (West Conshohocken, PA: ASTM).

3. ASTM D714, "Standard Test Method for Evaluating Degree of Blistering in Paints" (West Conshohocken, PA: ASTM).
4. ASTM D610, "Evaluating Degree of Rusting on Painted Steel Surfaces" (West Conshohocken, PA: ASTM).

Bibliography

Dean (Jr.), S.W. "Inhibitor Type." *MP* 20, 11 (1981): pp. 47-51.

Kofira, N. Technical development manager, Halox Co., Hammond, Indiana.

Lenard, D.R. and J.G. Moors. "The Effects of Vapor Phase Corrosion Inhibitors on the Galvanic Corrosion of Aluminium." *Corr. Sci.* 34, 5 (1993): pp.871-880.

Metal Handbook: Corrosion. Vol 13. New York, NY: ASM International, 1987, pp. 524-25.

Miksic, B.A. "Use of Vapor Phase Inhibitors for Corrosion Protection of Metal Products." CORROSION/83, paper no. 308. Houston, TX: NACE, 1983.

Miksic, B.A, M. Tarvin, M. and G.R. Sparrow. "Surface Analytical Techniques in Evaluation of the Effects of Vapor Phase Organic Corrosion Inhibitors on Surface Chemistry of Metals." CORROSION/89, paper no. 607. Houston, TX: NACE, 1989.

Trabanelli, G. and V. Carassiti. *Advances in Corrosion Science and Technology*. Vol 1. M.G. Fontana and R.W. Stachle, eds. Plenum, NY: Springer, 1970, pp. 186-188.

Wrangl'n, G. *An Introduction to Corrosion and Protection of Metals*. New York, NY: Chapman & Hall, 1985, pp. 165-173.

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