

Ron Camp, Cortec Corporation, investigates the use of vapour phase corrosion inhibitor technology with a non-zinc environmentally friendly metal complex inhibitor to improve the long-term corrosion protection of an acrylic coating applied direct-to-metal (DTM)

# Water-based coatings powered by NANO-VpCI

Today's waterborne coatings are steadily approaching to fulfil several requirements that are usually met by solventborne systems (good adhesion, corrosion resistance and improved weathering). Aqueous technologies are generally preferred over their solvent-based counterparts due to ease of application, lower VOCs and cost. However, waterborne coatings still struggle to provide long term protection for metals in extremely corrosive environments. Through research it has been found that combining Vapor Phase Corrosion Inhibitors (NANO-VpCI) with a non-zinc environmentally friendly metal complex inhibitor, will significantly improve the long-term corrosion protection of acrylic paints on steel substrates; the combination of these inhibitors provides a synergistic multi-layer defence of corrosion resistance through passivation and film formation.

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 non-toxic inorganic corrosion pigment combined with NANO-VpCI technology in a waterborne acrylic protective 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, 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 reducing corrosion reactions) along with transferring water from the metal surface and preventing it and other corrosive electrolytes from coming in contact with the bare metal.

For steel to corrode, oxygen and water must be in direct molecular contact with the surface of the substrate (see figure 1).

### Equations 1

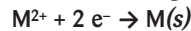
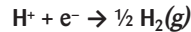
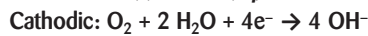
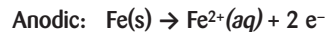
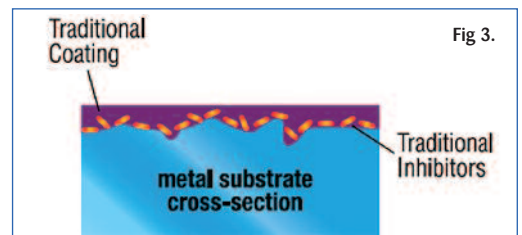
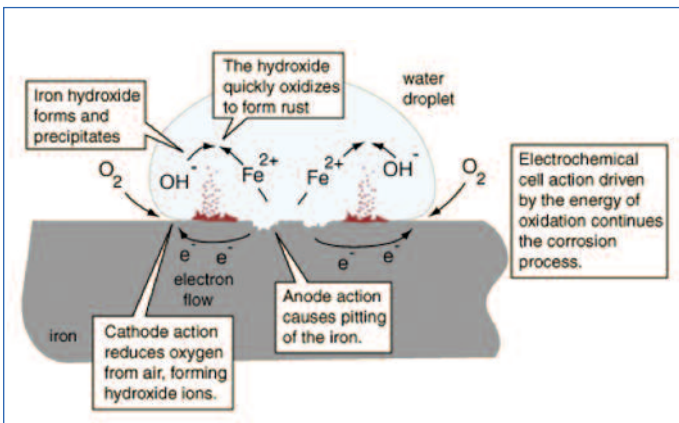


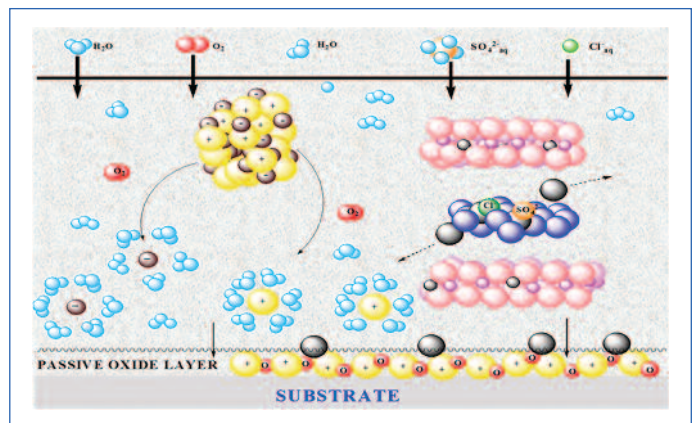
Fig 1. Below: Oxidation reaction of iron  
Fig 2. Below right



For this experiment, a non-toxic metal inhibiting pigment was used to provide passivation and ion scavenging protection. The inhibitor works through hydrolysis by dissociating and reacting with  $\text{Fe}^{2+}$  and  $\text{OH}^{-}$  ions to form  $\text{Fe}(\text{PO}_4)$  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 a ion scavenger, neutralising corrosive species such as  $\text{Cl}^{-}$  and  $\text{SO}_4^{2-}$  limiting their aggressive behaviour toward metal corrosion (see 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, which are entry points for micro-corrosion that can expand and lead to coating failure (see figure 3).

To improve the corrosion performance of the coating, NANO-VpCI (Vapor Phase Corrosion Inhibitors) were added to the matrix. The blend of vapour 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 (see figures 4 & 5).



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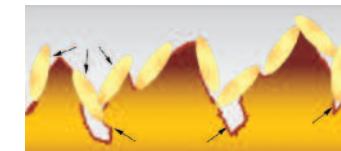
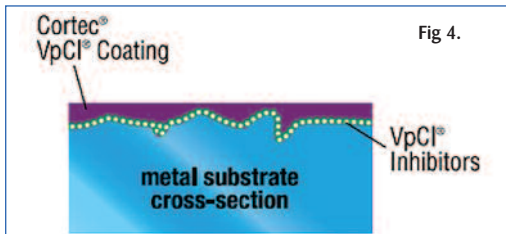
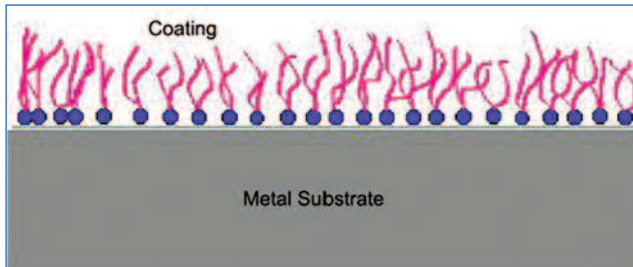


Fig 5.

Fig 6.



The mechanism of the NANO-VpCI's involves two parts; the first is the transport of the inhibitor to the metal surface and the 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 on to 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 on to passivating layers as well (see figure 6).

At higher concentrations, NANO-VpCIs 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-VpCI with a non-toxic metal complex inhibitor produced 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-crosslinking 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 (4in x 12in (102mm x 305mm)) panels using a wire wound drawdown rod to produce ~2.0mils of dry film thickness. The carbon steel specimens were prepared in accordance with ASTM B117 salt spray testing method.

After reaching full cure (seven days at ambient temperature), the panels were scribed as explained in method ASTM D1654. All backs and edges of the panels were taped to prevent corrosion creep. They were then placed into a 5% NaCl salt fog chamber for environmental testing for up 520hr. After 520hr, each sample was rinsed, scraped and rated for creep (ASTM D1654), blistering (ASTM D714) and degree of rusting (ASTM D610). 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-VpCI 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  $\leq 192$ hr in the salt chamber (Failure  $\geq 3$ mm creep from scribe). The salt vapours were able to quickly penetrate the film's barrier, which leads to blistering and loss of adhesion causing the underlying substrate to corrode (see figure 8).

Results in figure 9 shows the coating made using only the non-toxic 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 coat-

Fig 7. Control Sample 540hr of continuous salt spray

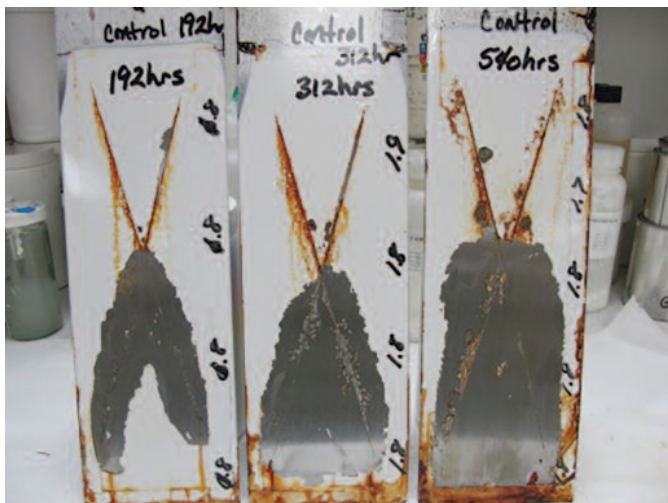
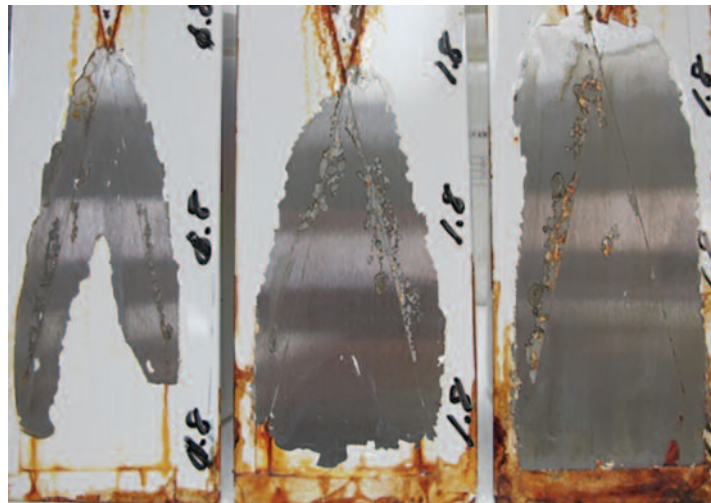


Fig 8. Close-up of fig 7



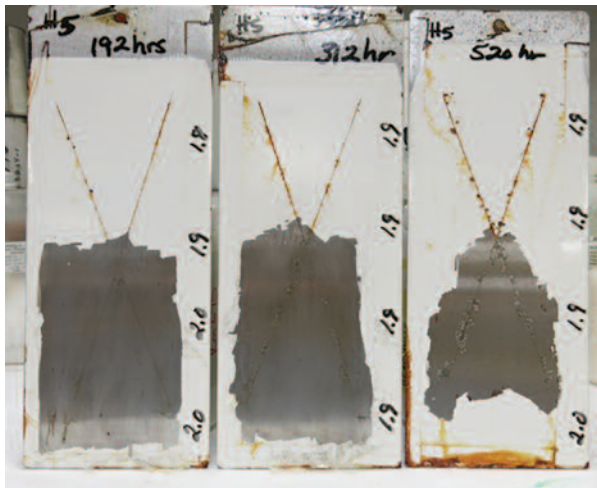


Fig 9. Sample containing eco-friendly pigment inhibitor

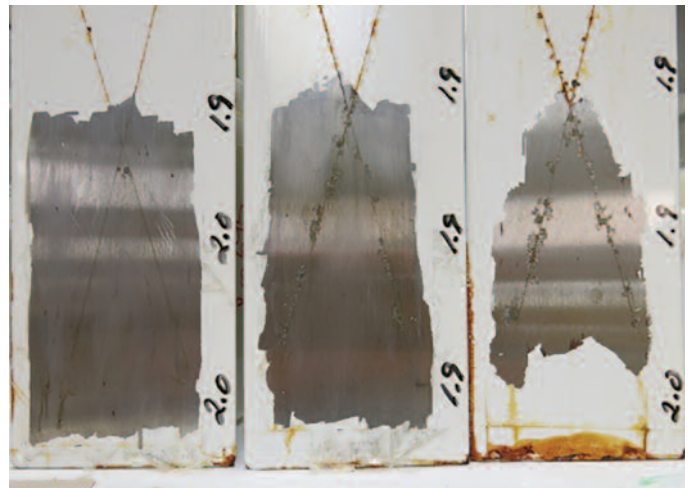


Fig 10. Above right: Close-up of fig 9

ing failed  $\leq 520$ hr in the salt spray chamber (see figure 10).

Figure 11 shows the results for the sample containing both the NANO-VpCI and eco-friendly pigment inhibitor that passed 520hr. 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 VpCI to migrate underneath the micro-gaps 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 (see figure 12).

**CONCLUSION**

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

Through research it has been found that combining Vapor Phase Corrosion Inhibitors (NANO-VpCI) with a non-toxic 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 defence of corrosion resistance through passivation, ion-scavenging and film formation.

**References**

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This paper was presented at the Advances on CoatingsTechnology – ACT'14 conference, organised by Paint and Plastics Department of the Institute for Engineering of Polymer Materials and Dyes on October 21-23, 2014 in Sosnowiec, Poland

Fig 11. Sample containing NANO-VpCI and eco-friendly pigment inhibitor

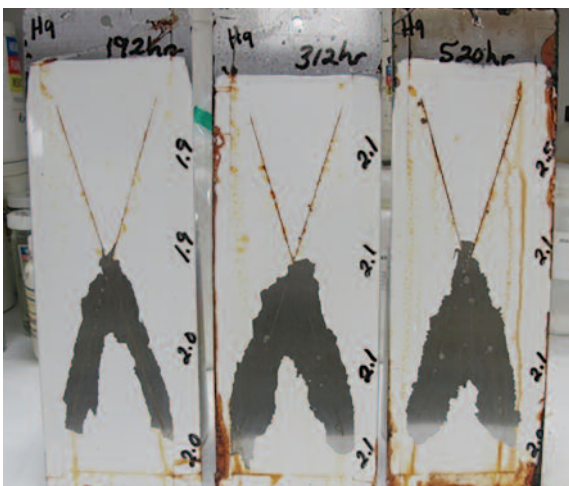


Fig 12. Close-up of fig 11

