

Volatile Corrosion Inhibitor Coatings

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Volatile corrosion inhibitors (VCIs) are organic materials that protect metals against corrosion by emitting vapors. This study shows that VCIs, combined with sulfonates (contact corrosion inhibitors), can retard corrosion in several different coating systems.

Coatings applied directly to metals normally use conventional corrosion inhibitor pigments such as zinc, aluminum, zinc oxide (ZnO), modified ZnO, and calcium ion-exchanged amorphous silica gel.

Using corrosion inhibitor pigments has several disadvantages. Some pigments contain metals that are toxic. Several, including metallic zinc, have high densities and settle. A number of pigments react with the resins in the coating. Additional pigmentation also requires added wetting agents that may affect corrosion resistance.

Volatile corrosion inhibitors (VCIs) are unique. They are organic compounds that protect metal surfaces by emitting a vapor such as an amine-based compound. The nitrogen on the amine has two electrons that are attracted to the polar metal surface. Once it is attracted to the metal, the rest of the molecule is very hydrophobic and repels water to significantly retard corrosion.

B.A. Miksic, et al.,¹⁻³ and Y.I. Kuznetsov, N.N. Andreev, and their

colleagues⁴⁻⁷ studied several amines, their derivatives, and imines used as VCIs. VCIs migrate from the coated area to the unprotected metal area. Metals coated with these VCI paints corrode very little in scribed areas since the films are self healing—the VCI evaporates and redeposits itself where the coating has been scratched. Many VCI coatings also contain other corrosion inhibitors to enforce the corrosion-resistance process.

I.L. Rosenfeld, et al.,⁸ and N.N. Andreev⁹ measured corrosion inhibition by using saturated vapor pressure. N.N. Andreev also used x-ray photoelectron spectroscopy to show the formation of a protective layer by vapor-phase transfer.⁴ B.A. Miksic, et al., developed surface analysis methods using electron spectroscopy for chemical analysis (ESCA), x-ray photoelectron spectroscopy (XPS), secondary-ion mass spectroscopy (SIMS), and ion scattering (ISS).¹⁰

VCIs have been used for years to temporarily protect metals from corrosion in extreme conditions found on automobile underbodies, offshore drilling decks, storage tanks, naval vessels,¹¹⁻¹² and in the petrochemical industry.¹³

VCIs formulated with standard resins in coatings have largely been ignored for use in industrial maintenance coatings. The reasons VCIs have not been used in coatings include:

- Many are temporary films because they can be removed easily.
- Some VCI coatings are soft, tacky, or even oily.
- VCIs have been used at fairly low levels in conventional industrial coatings. Higher levels may be needed to show the self-healing effect.
- Corrosion protection may not be the only requirement in a coating. Color limitation can be a concern, film hardness may be important, or a high gloss may be needed.

There are many ways to circumvent these limitations. Even though these coatings can easily be removed, they can be permanent where high abrasion

resistance is not a concern. Modifying typical industrial solvent-based coatings with VCIs is possible.

Waterborne coatings can also be modified with VCIs. VCIs are solvent- and water-soluble compounds that can be incorporated into waterborne coatings by emulsification, adding co-solvents, or simply dissolving them in water. Tack can be eliminated by adding pigments, waxes, hard resins, or curing agents in some cases. Care must be used to maintain good adhesion and compatibility in these situations.

Experimental Procedure

This study examines four temporary VCI coatings, one permanent epoxy VCI coating, two typical epoxies with no VCIs, and a waterborne alkyd with no VCIs. The VCI waterborne alkyd formulations are direct comparisons to a standard waterborne alkyd with the same resin, driers, and cosolvent.

MATERIALS

- **VCI petroleum-based coating:**

A proprietary blend of oxidized petrolatum, calcium salts blended with a low level of petroleum sulfonate, amine carboxylates, and mineral spirits.

- **VCI latex coating:** Acrylic latex, calcium salt of organo sulfonic acid, and amine carboxylates.

- **VCI solvent-based epoxy:** Bisphenol A epoxy with aliphatic amine, a blend of oxidized petrolatum, calcium salts blended with a low level of petroleum sulfonates, amine carboxylates, and mineral spirits.

- **15/32% VCI-modified water-based alkyds:** Engineered Polymer Solutions (EPS). An EPS 2601 alkyd, calcium salt of an organo sulfonic acid, and an amino carboxylate. Table 1 shows the formulation.

- **Water-based alkyd:** EPS 2601 (Table 1).

- **Typical epoxy coating:** Bisphenol A, an aliphatic amine with a standard corrosion pigmentation, and other pigments. LX07521 high-solids epoxy primer (Davis-Frost, Inc.).

TABLE 1

WATERBORNE ALKYD FORMULATIONS

Material	Manufacturer	Control	15% VCI	32% VCI
EPS-2601 (78%)	EPS	54	48	38.9
12% Mn	Condea	1	1	0.8
Active-8	R.T Vanderbilt	1	1	0.8
Sag 5440 defoamer	Union Carbide	0.8	0.8	0.7
Water		43.2	38.6	35.1
VCI-M (61%)	Cortec	10.6	23.7	
Totals		100	100	100

TABLE 2

ASTM B 117. 500-H SALT SPRAY RESISTANCE

Type	Film Thickness (mils/ μ m)	Corrosion Rating ^(A)	Scribe Rust ^(B)
VCI latex	2.2/56	10	10
VCI epoxy	1.7 to 1.9/43 to 48	9	9
VCI petroleum	1.5 to 1.9/38 to 48	8	9
Water-based alkyd	1.7 to 1.8/43 to 46	5	3
15% VCI-modified water-based alkyd	1.9/48	8	10
32% VCI-modified water-based alkyd	1.6 to 2.1/41 to 53	8	10
Solvent-based epoxy	2.0 to 2.2/51 to 56	7	5
Zinc-rich solvent-based epoxy	1.9 to 2.4/48 to 61	0	^(C)

^(A)ASTM D 1654-92 Procedure B rating of unscribed areas

10 = no corrosion, 5 = 11 to 20% corrosion, 0 = 75% and over.

^(B)ASTM D 1654-92 Procedure A rating of failure at scribe.

10 = no creepage, 5 = 0.125 to 0.1875 in. (0.32 to 0.48 cm), 0 = 5/8 or more mean average.

^(C)Entire surface corroded. Creepage could not be evaluated.

- **Zinc-rich epoxy primer:** Bisphenol A, aliphatic amine with a high level of zinc pigment, 3921 epoxy (Belzona[®]).

SAMPLE PREPARATION

All epoxy coatings were given a 1-h induction period after mixing. The coatings were drawn down using a drawdown bar on cold-rolled steel to a dry-film thickness (DFT) of 1.5 to 2.5 mils (38 to 63 μ m). They were air-dried for 7 days at room temperature before testing them in a salt spray cabinet (ASTM B-117) (Tables 2 and 3). All coatings were scribed with a vertical line.

Results

All of the VCI-modified coatings are softer than standard non-VCI-modified coatings. VCI coatings, however, offer better corrosion resistance (Table 2). The VCI solvent-based epoxy and the VCI petroleum-based coating were still in good condition with <5% corrosion after 1,000 h (Table 3 and Figure 1).

VCI TEMPORARY COATINGS

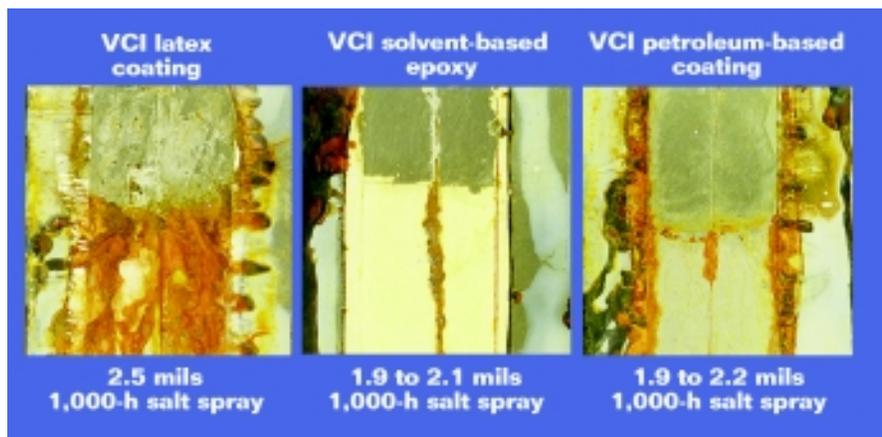
Two temporary coatings were tested: a VCI latex and a VCI petroleum-based coating. After 500 h of salt spray testing, both showed very strong VCI effect and no corrosion at the scribe (Table 2 and Figure 2). After 1,000 h of salt spray, the temporary VCI coatings began to fail (Table 3 and Figure 1). This effect is most noticeable with the VCI latex, which shows the greatest change. It went from no corrosion at 500 h to ~50% corrosion at 1,000 h in the salt spray cabinet.

The petroleum-based temporary coating containing VCI showed only a minor degree of corrosion at 1,000 h (Table 3 and Figure 1). This coating's more hydrophobic nature is the reason for the significantly better results.

VCI PERMANENT COATING

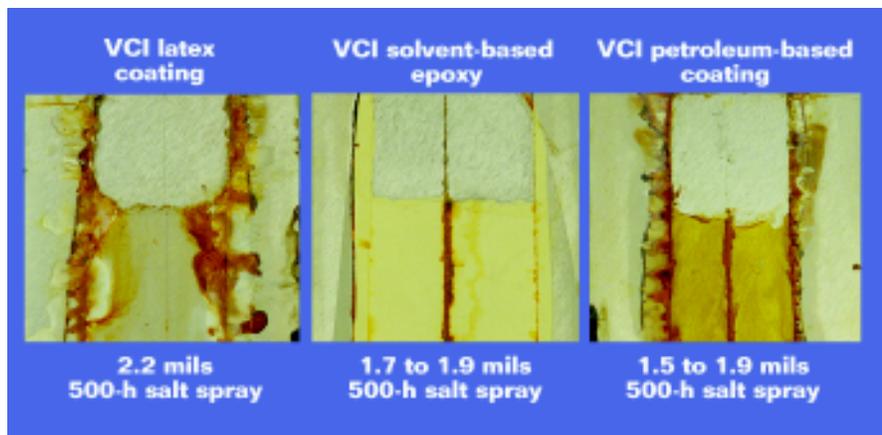
The VCI solvent-based epoxy showed the best corrosion resistance of all coatings tested. It is considered a

FIGURE 1



The VCI solvent-based epoxy and VCI petroleum-based coating had <5% corrosion after 1,000 h in a salt spray test.

FIGURE 2



After 500 h of salt spray testing, a VCI latex and VCI petroleum-based coating showed no corrosion at the scribe.

TABLE 3

ASTM B 117. 1,000-H SALT SPRAY RESISTANCE

Type	Film Thickness (mils/ μ m)	Corrosion Rating ^(A)	Scribe Rust ^(B)
VCI latex	2.5/64	1	6
VCI epoxy	1.9 to 2.1/48 to 53	8	7
VCI petroleum	1.9 to 2.2/48 to 56	8	7
Water-based alkyd	1.6 to 1.7/41 to 43	1	4
15% VCI-modified water-based alkyd	1.4 to 1.6/36 to 41	0	7
32% VCI-modified water-based alkyd	2.1 to 2.4/53 to 61	4	6
Zinc-rich solvent-based epoxy	2.0 to 2.3/51 to 58	0	(C)
Solvent-based epoxy	2.0 to 2.4/51 to 61	7	(D)

^(A)ASTM D 1654-92 Procedure B rating of unscribed areas. 10 = no corrosion, 5 = 11 to 20% corrosion, 0 = 75% and over.

^(B)ASTM D 1654-92 Procedure A rating of failure at scribe.

10 = no creepage, 5 = 0.125 to 0.1875 in. (0.32 to 0.48 cm), 0 = 5/8 or more mean average.

^(C)Coating delaminates when dried.

^(D)Entire surface corroded. Creepage could not be evaluated.

permanent coating, although it is somewhat soft at <6B pencil hardness. The scribe corrosion resistance was also very good (Tables 2 and 3 and Figures 1 and 2).

VCI WATER-BASED ALKYDS

Two waterborne VCI-modified alkyd coatings were run as a direct comparison to a waterborne alkyd without any VCIs (control). These formulations were not optimized—they were prepared simply to show the advantages of using VCIs in waterborne alkyds.

At 500 h of salt spray exposure, the 15 and 32% VCI-modified water-based alkyds showed no scribe rust compared to considerable rust on the control (Table 2 and Figure 3). The control did not have pronounced scribe rust; however, there was considerable general rust near the scribe. At 1,000 h, there was significantly more corrosion with all waterborne alkyds. Highly optimized formulations may have provided good protection. This alkyd also may not be able to last 1,000 h at <2 mils (51 μ m) thickness.

NON-VCI EPOXY COATINGS

Epoxy coatings are generally very good primers. In this study, two off-the-shelf epoxies were tested in the salt spray cabinet. One zinc-rich primer failed severely after 500 h in the salt spray cabinet (Table 2 and Figure 4). Another solvent-based epoxy delaminated after 1,000 h of salt spray exposure and began to rust at the scribe (Table 3 and Figure 5). The manufacturers recommend that topcoats should be used with these primers to maximize coating performance. However, having a primer with excellent corrosion resistance alone is an advantage. See the VCI epoxy shown in Tables 2 and 3.

Conclusions

The VCI coatings evaluated here are highly modified standard latex, epoxy, alkyd, and petroleum-based coatings

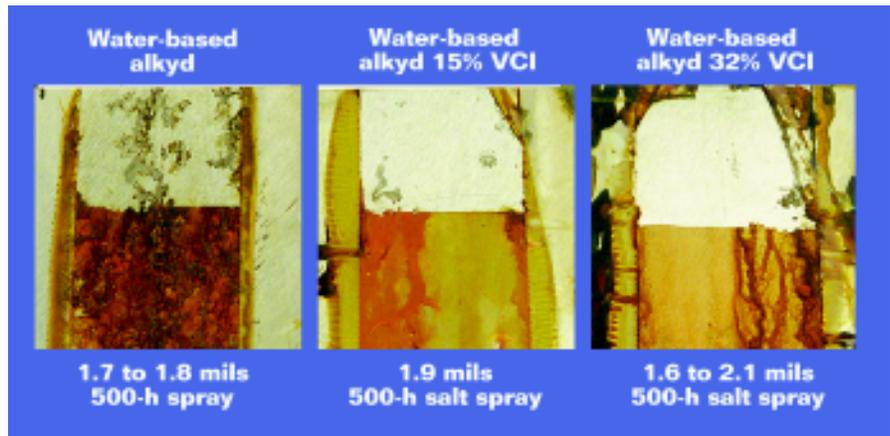
that have excellent corrosion resistance. They can be used for many practical applications based on end use, environment, cost, and stability.¹⁴ VCI coatings are an alternative to coatings containing corrosion-inhibiting pigments, although they can be used with such pigments.

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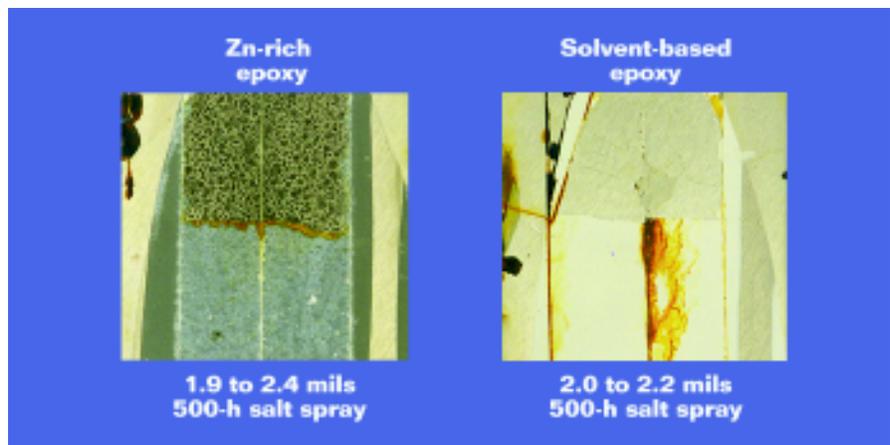
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FIGURE 3



At 500 h of salt spray exposure, the 15 and 32% VCI-modified water-based alkyds performed better than the control.

FIGURE 4



This zinc-rich primer failed after 500 h in the salt spray cabinet.

FIGURE 5



A solvent-based epoxy delaminated after 1,000 h of salt spray exposure.