

# Environmentally Friendly VCIs

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**Volatile corrosion inhibitors (VCIs) have evolved over the years to serve as effective protection for metals exposed to marine environments, chemical processing, metalworking, and many other corrosive conditions. This article discusses a new class of nontoxic and nonpolluting VCIs that can be safely used in environmentally sensitive areas.**

Originally developed to protect boilers and piping systems of ships to be mothballed, the volatile corrosion inhibitor (VCI) has been modified over the years

to protect electronics, packaged items, reinforced concrete, coated metals, and metalworking fluids.<sup>1-8</sup> Innovations in VCI technology have generated a new class of VCI chemicals that not only provide excellent protection to metal surfaces, but also protect the environment. In addition to being cost-effective, easy to apply, and durable, VCIs now are used effectively in environmentally sensitive areas because they are nontoxic and nonpolluting. They also offer the advantage of not requiring preparation of the metal surface prior to use, eliminating the removal and disposal requirements associated with petroleum-based

products typically used for cleaning.

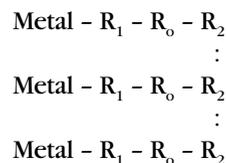
## VCI Chemistry

VCIs are a powerful tool in combatting atmospheric corrosion of metals and alloys. Because they are volatile at ambient temperature, VCI compounds can reach inaccessible crevices in

metallic structures. Protective vapors disseminate within an enclosed space until reaching equilibrium, which is determined by the partial vapor pressure of the VCI compound. The inhibiting process starts when the vapors contact the metal surface and condense to form a thin film of microcrystals. In the presence of even minute quantities of moisture, the crystals dissolve and develop strong ionic activity. This activity results in the adsorption of protective ions onto the metal surface, with the concurrent formation of a molecular film that serves as a buffer and maintains the pH level at its optimum range (5.5 to 8.5) for corrosion resistance.

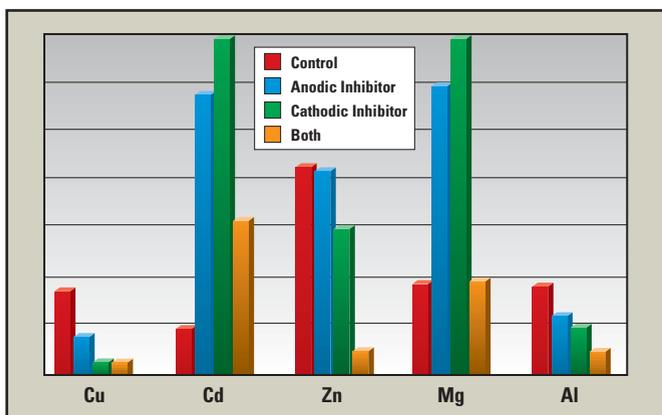
VCIs were originally developed to protect ferrous metals in tropical environments; however, recent developments in VCI chemistry are based on the synthesis of compounds that provide general protection (i.e., they protect most commonly used ferrous and nonferrous metals and alloys) (Figure 1). Electrochemical behavior investigations show that these VCI compounds belong to mixed or "ambiodic" inhibitors capable of slowing both cathodic and anodic corrosion processes. The reduction of the cathodic reaction results from a decrease in oxygen concentration caused by the formation of an adsorption film that acts as a diffusion barrier for oxygen. Strong inhibition of the anodic reaction results from the inhibitor's two acceptor-donor adsorption centers that form a chemical bond between the metal and the inhibitor. Adsorption of mixed VCI compounds changes the energy state of metallic ions on the surface, diminishing the tendency of metal to ionize and dissolve.

The inhibition mechanism proceeds as follows:



The functional group ( $R_1$ ), linked to the nucleus ( $R_0$ ) of the inhibitor molecule, is responsible for establishing a stable bond with the metal surface and controls how firmly the inhibitor is adsorbed on the metal. The functional group ( $R_2$ ), also linked to the nucleus, controls the thickness and penetrability of the film, which is important in resist

FIGURE 1



Exposure of nonferrous metals to atmosphere containing VCI.

ing the penetration of aggressive ions. As the inhibitor molecules are adsorbed on the metal surface, the R<sub>2</sub> groups form a continuous line of defense to protect the metal from corrosive species.

Active ingredients in VCIs usually are products of a reaction between a weak, volatile base and a weak, volatile acid. Such compounds, although ionized in water, undergo a substantial hydrolysis that is relatively independent of concentration. The independence contributes to the stability of the inhibitor film under various conditions.

The vapor pressure of the inhibitor is significant in achieving vaporization of the compound. Too high a vapor pressure will cause the inhibitor to be released to such an extent that a protective concentration cannot be maintained. A low vapor pressure means the inhibitor is not used up as quickly, assuring more durable protection. Additional time is required, however, to reach the protective vapor concentration; this leaves the metal exposed to increased risk of corrosion during the initial period of saturation. The vapor pressure of VCIs depends upon temperature (Figure 2). Controlled and dependable vaporization results from the proper selection of VCI compounds so that the amount vaporized with temperature matches the kinetics of the corrosion reaction. Higher temperature increases a metal's tendency to corrode. Similarly, more inhibitive material evaporates at higher temperatures. VCIs can self-adjust to the aggressiveness of the environment over a wide temperature range.

## Corrosion and Environmental Testing

A VCI identified as "VCI A" was used in corrosion and toxicity tests. VCI A is made of amine carboxylates. The lower end of its melting point range is 188°C.

### VIA TEST METHOD MEASURES VCI EFFECTIVENESS

The Vapor Inhibiting Ability (VIA) test method commonly is used to measure the effectiveness of VCIs.<sup>9</sup> It rapidly assesses the protection offered by VCI products, which can be powders, liquids, or packaging products such as papers or plastic films. Figure 3 illustrates the VIA assembly used in testing the VCI A compound. In this test, car-

bon steel UNS G1018 (Fed. Steel Spec QQ-S-698) plugs (1.6-cm diameter, 1.3-cm long) were polished with a 240-grit silicon carbide (SiC) abrasive. The abraded surface was then polished with a No. 400 aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) paper at 90 degrees to the previous abraded marks. The plugs were cleaned with methanol (CH<sub>3</sub>OH), allowed to air dry, and placed in a desiccator.

Ten mL of a synthetic glycerin-water solution—with a specific gravity of 1.075 at 24°C to create a 90% relative humidity atmosphere—was introduced into the bottom of the test assembly. The investigators added 0.05 g of VCI A to a dish, which was placed on the bottom of the jar. A lid was placed on the jar and tightened. The junction of the glass and lid was sealed with tape. A control sample also was prepared, consisting of a jar containing only a steel specimen.

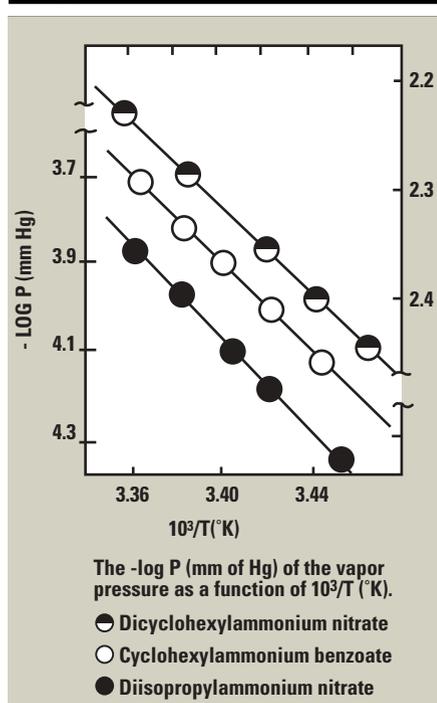
The assembly was exposed to a temperature of 24°C for 20 h. Cold water at a temperature of 4°C below the ambient temperature was added to the aluminum tubes until they were full. After 3 h, the water was removed from the tubes. The steel plugs were evaluated for signs of corrosion. In this test method, a visible change in the surface finish—such as pitting or etching—is considered corrosion. Stain alone does not indicate corrosion.

Table 1 provides the VIA test results. The control plug showed heavy corrosion; however, plugs placed in the presence of VCI A had no signs of corrosion. Figure 4 shows the plugs' appearance at the end of the test.

### ENVIRONMENTAL TESTING

Three environmental tests—bioaccumulation, biodegradation, and toxicity—were conducted on VCI A to determine its impact on the environment.

FIGURE 2



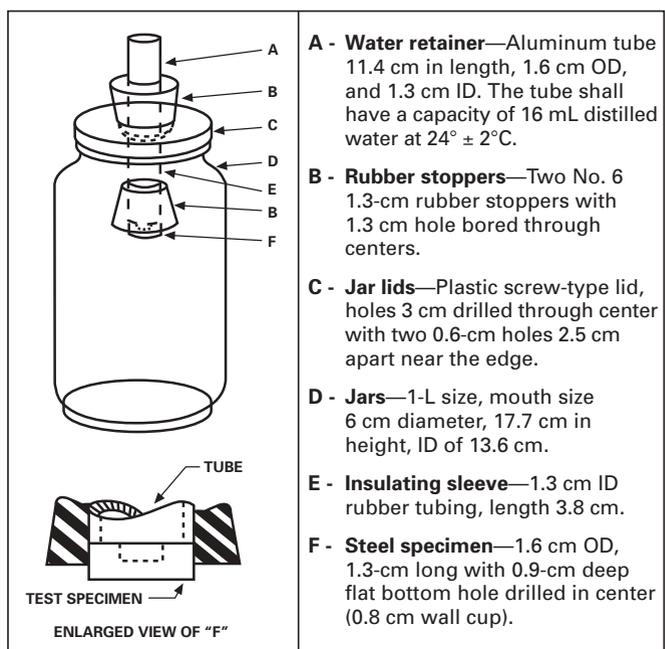
Dependence of saturated vapor pressure of VCIs upon temperature.

TABLE 1

## VIA TEST RESULTS

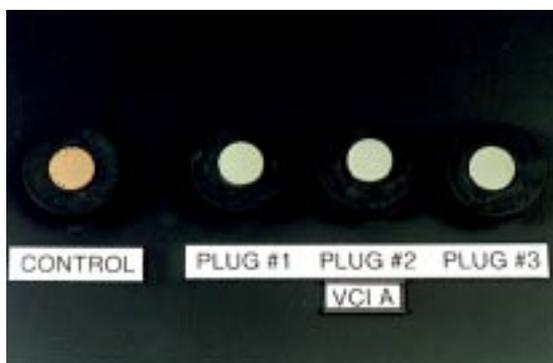
Sample	Results
Control	Fail
VCI A	Pass

FIGURE 3



VIA test assembly.

FIGURE 4



VIA steel plugs.

### BIOACCUMULATION

Bioaccumulation of substances within aquatic organisms can lead to toxic effects over long periods of time when actual water concentrations are low. The potential for bioaccumulation is determined by measuring the n-octanol/water partition coefficient of a specific chemical compound. In testing the VCI A compound, the partition coefficient  $P_{ow}$  was determined according to the Organization for Economic Co-Operation and Development (OECD) Guideline test number 117 [Partition coefficient (n-octanol/water), High-Performance Liquid Chromatography (HPLC) method].<sup>10</sup>

Table 2 shows the measured value of  $P_{ow}$ . With a value below zero, bioaccumulation is unlikely.

### BIODEGRADATION

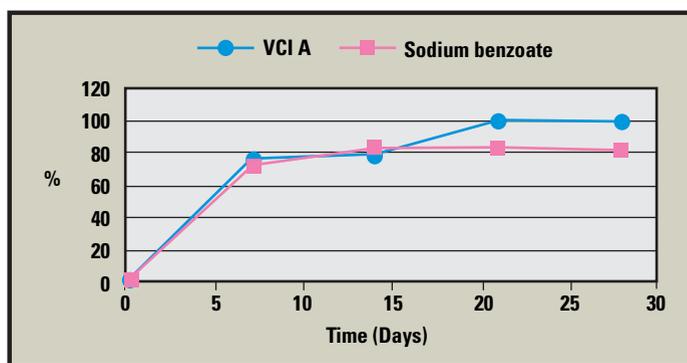
Biodegradation is a measure of the length of time over which a substance will remain in the environment. The biodegradability of VCI A was determined according to the OECD Guideline test number 306,<sup>10</sup> which is used primarily for biodegradation in marine environments. Chemical compounds are subjected to a 28-day biochemical oxygen demand (BOD-28) test. Degradation begins when 10% of the substance has been degraded. Rapid degradation is evidenced when at least 60% degradation of the substance is attained within 10 days of the start of degradation.

TABLE 2

### PARTITION COEFFICIENT

Test Method	Result	Limit
OECD 117 log $P_{ow}$	<0	<3

FIGURE 5



VCI A aerobic biodegradability.

Figure 5 shows the 28-day BOD value for VCI A. VCI A started to degrade rapidly. It was 10% decomposed in <2 days. It was 76% degraded on Day 7 and fully decomposed on Day 27. Ten days after the start of the degradation the level of degradation had surpassed 60%, indicating VCI A could be classified as a rapidly degradable substance. VCI A fully biodegraded as its BOD-28 value reached 100%.

### AQUATIC TOXICITY

Aquatic toxicity testing is conducted on organisms related to different levels of the food chain, including primary producers, such as algae; consumers, such as fish and crustaceans; and sediment reworkers, such as seabed worms. The toxicity usually is assessed by determining a 72- or 96-h  $EC_{50}$  for an algae species, a 48-h  $EC_{50}$  for a crustacean species, and a 240-h  $LC_{50}$  for a sediment reworker.  $EC_{50}$  is the effective concentration of a chemical substance necessary to have a negative effect on 50% of the aquatic organism population.  $LC_{50}$  is the effective concentration of a chemical compound required to kill 50% of the population.

The following tests were used to determine the aquatic toxicity of VCI A:

- Algae test—ISO/DIS 10253<sup>11</sup> (fourth working draft, “Water Quality—Marine Algae Growth Test with *Skeletonema costatum* and *Phaeodactylum tricornutum*) test method
- Crustacean test—ISO/DIS 14669-97<sup>12</sup> (“Water Quality—Determination of Acute Lethal Toxicity to Marine Copepods”) test method
- Sediment reworker test—ASTM E1367-90<sup>13</sup> (“Standard Guide for Conducting 10-Day Static Sediment Toxicity Tests with Marine and Estuary Amphipods”).

Tables 3, 4, and 5 present the results of the aquatic toxicity tests. According to the OECD 306 test guidelines,<sup>10</sup> the upper limit for acute toxicity measured as 72-h  $EC_{50}$  is 100 mg/L in the case of algae or other aquatic plants. The test results show that the 72-h  $EC_{50}$  for VCI A is 240 mg/L, indicating that VCI A is not classified as a chronic toxicant. Similar results are shown for consumers and sediment reworkers.

### CORROSION AND ENVIRONMENTAL TEST RESULTS

As the corrosion and environmental tests demonstrated, VCI A protects against corrosion while having no negative impact on the environment. The VIA test proved that VCI A could protect a steel specimen in a moisture condensing environment. The VCI source never came into contact with the steel plug, showing that VCI A reached the metal surface via sublimation. The results of the three environmental tests—low potential to bioaccumulate, quick biodegradability, and no acute toxicity to aquatic specimens—showed the low impact of VCI A on the environment.

### Environmentally Friendly Applications

Environmentally friendly VCIs are being used successfully in arenas requiring nontoxic and nonpolluting chemicals, such as the marine and chemical processing industries (Figure 6).

### NORTH SEA USE

A large Norwegian oil and gas producing company operating several offshore and onshore installations in the North Sea selected VCI technology as a cost-effective and environmentally friendly method of complying with stringent environmental regulations.

TABLE 3

## VCI A TOXICITY TO PRIMARY PRODUCERS

Concentration	Exposure Time (h)	Effect Concentration (mg/L)	Limit (mg/L)
EC <sub>50</sub>	72	240	≥100
EC <sub>90</sub>	72	680	—
No observed effect concentration	72	32	—

TABLE 4

## VCI A TOXICITY TO CONSUMERS

Concentration	Exposure Time (h)	Effect Concentration (mg/L)	Limit (mg/L)
LC <sub>50</sub>	48	100	≥100
LC <sub>90</sub>	48	220	—
No observed effect concentration	48	32	—

The company eliminated the use of an oil-water emulsion and its associated disposal costs and cleaning requirements, replacing it with VCI A for hydrotesting and preservation of internal surfaces of pipes and vessels. VCI A is used on large pipe systems on offshore platforms or smaller systems in refineries or on onshore oil and gas receiving stations.

VCI A was fogged inside the openings of recently hydrotested metering stations (Figure 7) at a ratio of 500 g/m<sup>3</sup>. The ends were capped to seal the installation, protecting the units for extended periods of time until they were dispatched and installed at their final destinations. After hydrotesting, an aqueous solution (usually at a concentration between 1% and 3.5%) of VCI A powder was sent to a storage tank and used again or simply discharged into the sea. VCI A applications also have been successfully used on onshore pipelines and pig-launching installations (Figures 8 and 9).

### CHEMICAL PROCESS INDUSTRY USE

VCIs have been applied in a number of chemical process industry services that involve enclosed atmospheres and require nontoxic and nonpolluting inhibitors. For larger equipment, such as tanks, boilers, and condensers, VCIs are applied in bulk powder form. The inhibitor vaporizes once it is introduced into the enclosure. The protective film continuously renews itself as the compound vaporizes and the vapors condense. The powder is applied by misting and, once applied, the enclosure is sealed and no additional measures (e.g., dehumidification, oxygen scavenging, etc.) are needed for the entire period of protec-

TABLE 5

## VCI A TOXICITY TO SEDIMENT REWORKERS

Concentration	Exposure Time (h)	Effect Concentration (mg/kg)	Limit (mg/L)
LC <sub>50</sub>	240	1,410	≥100
LC <sub>90</sub>	240	2,800	—
No observed effect concentration	240	1,014	—

tion. In situations when it is possible to seal the enclosure air-tight, the inhibitor is applied by first evacuating the enclosure and then repressurizing it to allow the powder to be drawn in.

The quantity of inhibitor needed to protect a given volume can be calculated from the following empirical formula:

$$Q = 0.0277VC \quad (1)$$

Where Q = total quantity of VCI powder, oz; V = volume of the enclosure to be protected, ft<sup>3</sup>; and C = confidence factor (2 to 3). The cost per unit of volume per year is nominally \$0.01 per ft<sup>3</sup>.

One or more VCI application devices in the form of a cartridge or tablet can be used to protect smaller enclosures (e.g., in electrical and electronic equipment). The device's chemical package usually contains a mixture of inhibitors. It also may contain a fungistat to control fungal growth and a volatile buffer to create a uniform pH on exposed metallic surfaces. It often is difficult to determine

FIGURE 6

VCI Performance in Industrial and Marine Atmospheres		
----- All corrosion rates in mils/y -----		
Metal	No Inhibitor	VCI Protected <sup>(A)</sup>
Aluminum (1000, 300, 5000 6000 series)	2.15	<0.25
Mild Steel	21.8	<0.13
HSLA (high-strength low-alloy steel)	1.2	0.08
Naval Brass	0.2 <sup>(B)</sup>	0.03
Titanium	0.0 <sup>(D)</sup>	0.0 <sup>(C)</sup>
Stainless Steels: 410	0.01 <sup>(D)</sup>	0.01 <sup>(E)</sup>
304	<0.1 <sup>(F)</sup>	0.01 <sup>(G)</sup>
301, 316, and 321	0.0 <sup>(H)</sup>	0.0 <sup>(H)</sup>
Copper	0.22 <sup>(F)</sup>	0.01 <sup>(G)</sup>

Notes:  
<sup>(A)</sup> NI-22790 formulation <sup>(B)</sup> Dezincification <sup>(C)</sup> Immune to attack; no pitting or weight loss observed <sup>(D)</sup> Pitting <sup>(E)</sup> Pitting reduced <sup>(F)</sup> Staining <sup>(G)</sup> No staining <sup>(H)</sup> Free from pitting and weight loss.

VCI performance in industrial and marine atmospheres.

FIGURE 7



Metering station.

**FIGURE 8**

Onshore pipeline installation.

**FIGURE 9**

Pig-launching installation.

the exact number of VCI devices necessary for protection because of the various shapes and sizes of enclosures and the varying conditions of storage. Typical devices protect a 1- to 40-ft<sup>3</sup> (0.03- to 1.13-m<sup>3</sup>) volume for 2 years. The actual number of devices needed to achieve saturation of vapors in a specific period of time and to maintain that saturation for 2 years is conventionally determined by the following equation:

$$N = (k_a)(k_p)(k_s)(N_o) \quad (2)$$

Where N = number of devices needed to protect a given volume under specific conditions;  $k_a$  = factor expressing the corrosiveness of the environment;  $k_p$  = factor expressing frequency of opening or breathability of the enclosure;  $k_s$  = factor expressing the shape of the enclosure; and  $N_o$  = number of VCI devices that are based on nominal volume of protection.

VCIs offer the chemical processing industry economic and procedural advantages. It is not necessary to prepare the metal surface prior to using VCIs because their vapors can penetrate to remote areas of an enclosure. Using VCIs also reduces the requirement to rigidly plan maintenance schedules because the compounds can protect dissimilar metals and perform in severe environments.

## Conclusions

VCIs are used in a wide range of situations where atmospheric corrosion damages exposed metals, including environmentally sensitive marine environments and the chemical processing industry. In addition to providing excellent corrosion protection and low toxicity levels, VCIs are cost-effective and long-lasting.

## References

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