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CORROSION PREVENTION AND CONTROL

FOCUS ON CORROSION PREVENTION WITH VOLATILE CORROSION INHIBITORS

Protection of Military Equipment Worldwide

Environmentally Friendly VCIs

Migrating Corrosion Inhibitors for Steel Rebar in Concrete

Fire Water System Protection



A Supplement to





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Corrosion Prevention and Control with Volatile Corrosion Inhibitors

Note that have been refined over the years to effectively fight corrosion inhibitors (VpCIs), and migrating corrosion inhibitors (VCIs), the related vapor-phase corrosion inhibitors (VpCIs), and migrating corrosion inhibitors (MCIs). Originally developed to protect boilers and piping of ships to be mothballed, VCIs now are being used to prevent corrosion in pipelines, military vehicles and equipment, cooling towers, concrete structures, storage tanks, electronics, packaging systems, and more.

Cortec Corp.—also celebrating a milestone anniversary in 2003—has been in the business of developing and applying VCIs, VpCIs, and MCIs for 25 years. Company researchers have authored numerous conference papers, technical briefs, and journal articles on the science and applications of these technologies, several of which are included here.

One article reveals how VCIs are being used effectively in environmentally sensitive areas because they are nontoxic and nonpolluting. Another provides details on laboratory and field applications of VpCI products that are being used by military organizations worldwide. An article on MCIs reveals how these inhibitors actually penetrate concrete to protect the supporting steel rebar within, while another describes how VpCIs provide protection from corrosion in wet and dry fire water pipe systems. An extensive literature research index is provided for those interested in learning more about these corrosion inhibitors and their applications.

Innovative corrosion control systems will continue to evolve as researchers find new and better ways to protect materials from the damaging—and sometimes devastating—effects of corrosion. By keeping pace with these technologies and relying on the expertise of corrosion professionals, organizations will improve operations, reduce costs, and help fulfill the crucial mission of NACE and its members to protect people, assets, and the environment from the effects of corrosion.

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report of a 2-year nationwide study released to the U.S. Congress in March of 2002,¹ the U.S. incurs billions of dollars in corrosion costs each year for reinforced concrete structures (e.g., highway bridges, waterways, ports, and drinking water and sewer systems). The annual direct cost of corrosion for highway bridges alone is estimated to be \$8.3 billion (Figure 1). Indirect costs related to traffic delays and lost productivity are estimated to exceed 10 times the direct cost of corrosion maintenance, repair, and rehabilitation.

ccording to the final

Previous studies have verified the benefits of using migrating corrosion inhibitors (MCIs), the importance of good concrete, and the significance of ingredients used to make the concrete for protection of reinforced concrete structures from corrosion.2-10 Steel reinforcing bars (rebar) embedded in concrete show high resistance to corrosion because the alkaline environment provided by the cement paste in the concrete promotes the formation of a protective ferrous oxide (FeO) film. The rebar's ability to remain passivated and protected from corrosive species, such as carbonation and chloride ions that can penetrate through the concrete pores to the rebar oxide layer, is influenced by the water-tocement ratio, permeability, and electrical conductivity of concrete. In highly corrosive environments, the passive layer will break down, leaving the rebar vulnerable to carbonation and chloride attack. In these environments. corrosion prevention is necessary.

Advancing MCI Technology

MCI technology was developed to protect the embedded steel rebar and the concrete structure. Recent MCIs are based on amino-carboxylate chemistry, with the most effective types of inhibitor interacting at the anode and cathode simultaneously.24 MCIs penetrate into the existing concrete to protect steel from chloride attack.⁶ The inhibitor migrates through the concrete capillary structure, first by liquid diffusion via the moisture normally present in concrete, then by its high vapor pressure, and finally by follow-

Migrating **Corrosion** Inhibitor **Protection of Steel** Rebar in Concrete

BEZAD BAVARIAN AND LISA REINER

Laboratory analysis determined the effectiveness of migrating corrosion inhibitors (MCIs) for reinforced concrete. Nyquist plots showed high polarization values for concrete treated with inhibitor. X-ray photoelectron spectroscopy (XPS) analysis confirmed that MCI migrated through the concrete. XPS depth profiling indicated that the inhibitor was able to suppress corrosion even in the presence of chloride. The effects of applying MCI directly to the rebar into the concrete were not apparent. Additional data are required to make any conclusion about the effectiveness of an application method.

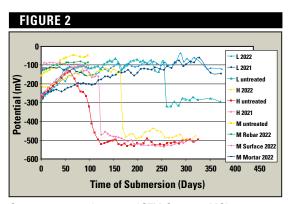
ing hairlines and microcracks. The diffusion process requires time for the MCI to reach the rebar and form a protective layer.

MCIs can be incorporated into concrete batches as an admixture or can be used by surface impregnation of existing concrete structures. With surface impregnation, MCIs diffuse into the deeper concrete layers to inhibit the onset **FIGURE 1** \$0.5 billion Maintenance painting of steel bridges \$2.0 billion Maintenance and cost of capital for concrete bridge decks \$3.8 billion Replace structurally deficient bridges over the next 10 years \$2.0 billion Maintenance and cost of capital for concrete substructures (not including decks)

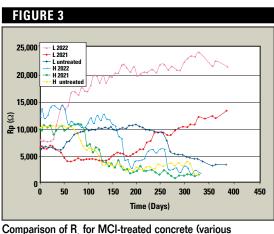
Distribution of the estimated \$8.3 billion annual direct cost of corrosion for highway bridges.¹

of steel rebar corrosion. Bjegovic and crete structures.² Laboratory tests have Miksic demonstrated the effectiveness of MCIs over 5 years of continuous testing.24 They also showed that the MCI admixture is effective in repairing con-

also proven that MCIs migrate through the concrete pores to provide rebar with protection from corrosion even in the presence of chlorides.^{4,5}



Corrosion potential vs time, ASTM C876-91, MCI 2022 and 2021 compared with unprotected concrete (various concrete densities).



densities) with untreated samples.

Concrete Density and MCI Application Method

The rate of MCI migration in part depends on the density and permeability of the concrete. A high-density concrete that impedes the movement of corrosive species to the surface of the rebar may also prevent the inhibitor from reach-

TABLE 1

TEST SAMPLES

Concrete Sample (0.5 water/cement ratio)	Concrete Density	MCI	Application Method
A (2 samples)	Low (L) (2.08 g/cm ³)	2022	MCI-treated concrete surface
B (2 samples)	Low (L) (2.08 g/cm ³)	2021	MCI-treated concrete surface
C (1 samples)	Low (L) (2.08 g/cm ³)	Untreated	No MCI application
D (2 samples)	High (H) (2.40 g/cm ³)	2022	MCI-treated concrete surface
E (2 samples)	High (H) (2.40 g/cm ³)	2021	MCI-treated concrete surface
F (1 samples)	High (H) (2.40 g/cm ³)	Untreated	No MCI application
G (2 samples)	2.24 g/cm ³	Untreated	No MCI application
H (2 samples)	2.24 g/cm ³	2022	MCI-treated concrete surface
I (2 samples)	2.24 g/cm ³	2022	MCI-coated rebar cast in concrete
J (2 samples)	2.24 g/cm ³	2022	MCI-mortar mixture applied to concrete surface

ing the rebar surface. To determine the effects of concrete density and application method when using MCIs, 10 specimens comprising three concrete densities were compared for corrosion inhibition properties. Six concrete samples were prepared with corrosion inhibitors using different application methods (Table 1). Two concrete samples were left untreated as references.

Concrete samples were cast (dimensions 20 x 10 x 10 cm) using commercial-grade silica, Portland cement, fly ash, and limestone (concrete mixture ratio: 1 cement/2 fine aggregate/4 coarse aggregate). Low-density concrete at 2.09 g/cm³ (130 lb/ft³) was prepared with a 0.5 water/ cement ratio with a concrete mixture for 2.5 ft3 (20.4 kg cement, 40.8 kg fine aggregate, 81.7 kg coarse aggregate, and 10 kg water). Medium-density concrete at 2.24 g/cm3(140 lb/ ft³) was batched using a 0.50 water/cement ratio, with a

concrete mixture for 2.5 ft³ (21.8 kg cement, 43.6 kg fine aggregate, 78 kg coarse aggregate, and 10.9 kg water). High-density concrete at 2.40 g/cm³ (150 lb/ft³) was batched using a 0.50 water/ cement ratio with a concrete mixture for 2.5 ft³ (24 kg cement, 47 kg fine aggregate, 94.4 kg coarse aggregate, and 11.8 kg water).

The maximum aggregate size was ~1/2 to 5/8 in. (12 to 15 mm). Gradation was uniform. Coarse aggregate was crushed stone, natural gravel (river gravel), quartzite, quartz, and sandstone. Fine aggregate primarily comprised sand, quartz, and some clay. The water/ cement ratio was moderately low at ~0.50. Paste content was moderate and unhydrated cement grains rarely were found in pastes. The degree of consolidation was good, the contacts of matrix with aggregates were relatively close, and some minor openings were visible on the polished or broken surfaces. The degree of air entrainment was measured to ~1.2 to 1.5% (28 to 30 mm²/mm³ or 700 in.²/in.³). Compressive strengths were ~3,100 to 3,950 psi (21 to 27 MPa).

Prior to being placed in the concrete sample, the steel rebar (class 60) was exposed to 100% relative humidity to initiate corrosion. The rebar was covered with a 1-in. (2.5-cm) layer of concrete. On all samples, a copper/copper sulfate (Cu/CuSO₄) reference electrode was used, with an Inconel 800[†] metal strip serving as the counter electrode. The concrete samples were partially immersed (87.5% of the height) in a 3.5% sodium chloride (NaCl) solution. The top portion of the concrete sample was exposed to air.

Changes in the resistance polarization (R_p) and the corrosion potential of the rebar were monitored weekly using direct current (DC) electrochemical and alternating current (AC) electrochemical impedance spectroscopy over a 450day period to determine the effectiveness of the MCI products. After 450 days of immersion in NaCl solution, several concrete samples were cut open and the rebar removed for x-ray photoelectron spectroscopy (XPS) analysis to verify inhibitor migration through the concrete and its adherence to the rebar structure.

Investigation Results

The assessment of the corrosion inhibitors for the three concrete densities was based on open circuit potential (corrosion potential) values, R_p values, and XPS analysis.

OPEN-CIRCUIT POTENTIALS

According to ASTM C876,¹¹ if the open-circuit potential is –200 mV or less negative, a 90% probability exists that

[†]Trade name.

no reinforcing steel has corroded. Corrosion potentials more negative than -350 mV are assumed to have >90% likelihood of corrosion. Corrosion potentials for the high-density samples (H2021, H2022, H untreated) were ben -400 mV and -600 mV after 128 days of immersion in NaCl (Figure 2). The untreated control sample (L untreated) had a corrosion potential of -295 mV at the end of testing. MCI-treated, low-density samples (L2022, L2021) had corrosion potentials ranging from -120 mV to -145 mV. The inhibited samples with a density of 2.24 g/cm3 showed corrosion potentials between -48 mV to -175 mV during the first 130 days of testing, regardless of the application method. The low-density samples had significantly less negative corrosion potentials, indicating good passivation.

POLARIZATION RESISTANCE

Figure 3 shows the R_p values at the end of testing to be from 13,000 to 22,000 Ω for the low-density samples treated with MCI. The high-density concrete showed significantly less corrosion inhibition, with R_n values ranging from 1,000 to 2,000 Ω . R_p values for non-treated samples ended at 3,170 Ω for low-density samples and 1,200 Ω for high-density concrete. Changes in R_p value were not immediately observed, indicating that diffusion of corrosive species or MCIs into the concrete requires an induction period (~120 days). Figure 4 illustrates the substantial difference between low-density and high-density concrete samples.

XPS ANALYSIS

Figure 5 shows the XPS spectra for two rebar removed from the MCI-treated samples after 450 days. The inhibitors had penetrated the concrete layer, reaching the rebar and slowing down corrosion. Figure 6 illustrates the depth profiling of steel rebar removed from MCI-treated concrete samples, indicating that a 140-nm layer of amine-rich compound (amine-based MCI) was detected on the rebar's surface. Chloride was also found on the rebar surface, with deposits varying from 0.99 and 0.84 wt% concentration for MCI 2022 and MCI 2021, respectively. The XPS results showed that MCI and corrosive species (chloride ions) had migrated through the concrete, but the MCI had neutralized the corrosive species and protected the steel rebar.

Conclusions

Lower-density concrete samples provided an easier path for the inward diffusion of MCI, resulting in faster corrosion retardation. The MCI products were found to offer protection for the steel rebar by suppressing the chloride ions. They are capable of inhibiting corrosion in aggressive environments, such as seawater. MCIs continue to demonstrate their effectiveness in protecting reinforced concrete structures.

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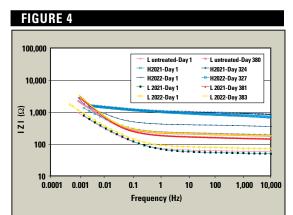
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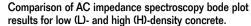
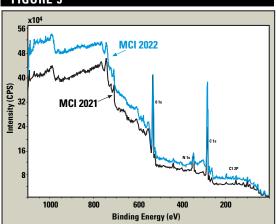
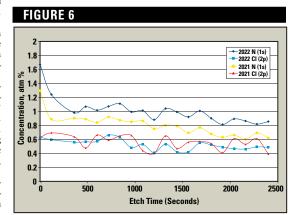


FIGURE 5



XPS spectrum of steel rebar removed from MCI-treated concrete after 450 days of submersion. Large area (1,000 by 800 mm) survey scan. Lens mode electrostatic; resolution pass energy –160; anode: Mg (150 W).



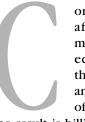
XPS depth profiles of steel rebar removed from MCI-treated concrete samples after 450 days of submersion (etched using 2kV argon ions).

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Corrosion Protection of Military Equipment Worldwide

ANNA M. VIGNETTI, LUKA MISKOVIC, AND TADIJA MADZAR

Corrosion damages billions of dollars of military assets every year. Military organizations evaluate and utilize a variety of preservation methods that protect equipment from corrosion without compromising war readiness. This article describes types of prevention employed by military organizations and details several laboratory and field applications of vapor phase corrosion inhibitor products and systems used successfully by military organizations worldwide.



orrosion significantly affects the performance of military equipment, shortens the time frame for use, and increases the risk of catastrophic failure.

The result is billions of dollars in lost assets each year and jeopardized war readiness. Military organizations worldwide continue to take steps to objectively evaluate different corrosion prevention methods in vehicles, aircraft, high-tech electronics, facilities, naval vessels, and weaponry.

Among the different corrosion prevention methods tested, vapor phase corrosion inhibitor (VpCI) technology continues to provide an effective, environmentally friendly, and relatively inexpensive method of controlling corrosion. VpCIs are chemical compounds that have significant vapor pressures that allow molecules to vaporize and then adsorb on metallic surfaces.¹⁻² When added in small concentrations, VpCIs effectively check, decrease, or prevent atmospheric corrosion caused by the reaction of the metal with the environment.

Corrosion Prevention Methods

Table 1 presents four methods currently employed by military organizations to prevent corrosion. They include products that block moisture and other atmospheric contaminants; products used to absorb moisture; alternatives, such as dehumidification; and VpCIs.

Laboratory and Field Experiments

LABORATORY TESTING

Specific laboratory testing for ASTM International and Military (MIL) Specification standard test procedures was conducted to support the successful use of VpCIs in field applications.

FINGERPRINT REMOVAL PROPERTIES TEST

Handling metal components can lead to corrosion as a result of the corrosive nature of the salts in human skin. Because it is difficult to ensure that hands are covered when handling metal equipment, a military test and specification was developed to test the ability to remove fingerprint oils and provide corrosion protection. Table 2 presents the procedure, and the results are shown in Table 3.

VpCI OIL BASE COATING TEST

A VpCI oil base coating was tested on carbon steel panels (SAE 1010) under highly humid conditions (ASTM D1748³), salt spray conditions (ASTM B117⁴), and cyclic environmental conditions (ASTM G85⁵). The test methods simulated the environment under which military equipment may be used or stored. Table 4 shows the results.

VpCI TEMPORARY SOFT COATING TEST

A VpCI temporary outdoor coating with self-healing properties was tested for various properties according to the military standard method, MIL-C-16173E⁶ Grade 1, Class 1. Table 5 presents the results.

FIELD APPLICATIONS

Many VpCI products and systems used to protect military equipment from

TABLE 1 CORROSION PREVENTION METHODS USED BY MILITARY ORGANIZATIONS

Corrosion Prevention Method	Product Type	Benefits	Disadvantages
Water-displacing products	Petroleum-based (light oils or thixotropic greases)	 Relatively inexpensive Water displacement Create a barrier coating on metal surfaces Excellent permanent protection 	 Costs increase with additives (e.g., contact inhibitors, extreme- pressure additives) needed to enhance protection High labor and material costs for application and removal of product Use of solvent-based cleaners for product removal makes these products unsafe for the worker and environment
Water-absorption products	Silica gel (dessicants)	 Economical alternatives for temporary protection Effective for storage and shipping Effective in electronic and electrical operations 	 Difficult to calculate specific moisture that will be present (i.e., requires more dessicant and inspection) Costs increase with the addition of more dessicant and inspections Airtight seal is required but difficult and expensive to achieve
Dehumidification	 Dehumidifier Vapor barrier bags 	 Can be successful if air flow to the metal is totally restricted Vapor barrier bags are excellent for one-time use (offer a sturdy multilayer film) Good way to protect electronics 	 Dehumidifier Electricity mandatory for dehumidifier and not available in remote locations Difficult to keep a seal on the metal object High cost of equipment and associated upkeep Vapor barrier bags High costs of materials and labor needed to create air- tight protection Not a good method to use during operations
VpCIs	 Anodic inhibitors (e.g., sodium nitrite [NaNO₂], dicyclohexylamine nitrite, sodium benzoate) Cathodic inhibitors Mixed inhibitors 	 Anodic inhibitors Prevent metal corrosion Cathodic inhibitors Slow cathodic reaction Precipate onto cathodic sites, restricting diffusion of corrosive species Mixed inhibitors Adsorbed onto metal surface, creating a monomolecular layer Monomolecular film acts as a buffer, maintaining pH at optimum range for corrosion resistance Provide a universal effect on corrosion process 	 Anodic inhibitors Negative effect on worker safety Negative effect on environment

TABLE 2 PROCEDURE PER MIL-C-15074,⁷ CORROSION PREVENTION, FINGERPRINT REMOVAL

Step	Procedure
1	Prepare fingerprint test solution (7 g sodium chloride [NaCl], 1 g urea [CO(HN ₂) ₂], 4 g lactic acid [C ₃ H ₆ O ₃], 1 L deionized water).
2	Place a pad of gauze on a flat dish and place 1.5 mL of fingerprint solution on pad.
3	Sand a rubber cork with sandpaper and rinse with deionized water.
4	Wash five steel panels with methanol (CH ₃ OH) and air dry.
5	Place fingerprint solution on panels using rubber cork and immediately place in an oven set at 121°C for 5 min.
6	Place one panel in boiling methanol for 2 min. Immerse a second panel in $1,1,1$ -trichloroethane (CH ₃ CCl ₃) for 1 min. Immerse three panels in a VpCI product for 2 min.
7	Place all panels in a dessicator with water for 24 h.
8	After 24 h, open the dessicator and visually evaluate the condition of the panels.

TABLE 3 MIL-C-15074, CORROSION PREVENTION, FINGERPRINT REMOVAL TEST RESULTS

Material	Results	Fingerprint Removal
Methanol	No corrosion	100%
1,1,1-trichloroethane	Severely corroded	0%
VCI-327	No corrosion	100%

TABLE 4

VpCI OIL BASE COATING TEST RESULTS

Environmental Test Condition	ASTM Standard Test Method	Coating Film Thickness	Test Duration
Humidity	D1748	2 mils (50 µm)	2,000 h
Salt Spray	B117	2 mils (50 µm)	170 h
Prohesion	G85	2 mils (50 µm)	500 h

TABLE 5

MIL-C-16173E, GRADE 1, CLASS 1 RESULTS FOR VpCI TEMPORARY SOFT COATING

Test	Test Method (Section)	Result
Material	3.2	Pass
Toxicity	4.8	Pass
Film characteristics	4.6.11.7	Pass
Solvent distillation endpoint	4.6.1	Pass
Discernibility	3.6	Pass
Stability	4.6.6	Pass
Recovery from low temperature	4.6.6.1	Pass
Uniformity	4.6.6.1.2 & 4.6.11.4	Pass
Storage stability	3.73	Pass
Flash point	4.6.2	Pass
Removability	4.6.10.1	Pass
Salt spray	4.6.11.4	Pass
Weather-accelerated	4.6.11.5	Pass
Flow resistance	4.6.15	Pass
Sprayability	4.6.7	Pass
Corrosion	4.6.8.1 & 4.6.8.2	Pass
Low-temperature adhesion	4.6.12	Pass
Drying	4.6.13	Pass

corrosion around the world have been tested, approved, and documented. The following field applications vary from simple corrosion protection to more sophisticated solutions.

VpCI PROTECTION FOR NASA

The U.S. National Aeronautics and Space Administration (NASA) successfully used a simple application of a VpCI coating to protect the O-rings in the space shuttles from corrosion caused by saltwater atmospheric contamination. The coating was approved under MIL-C-16173E (Table 5) to meet NASA's requirement to eliminate or reduce the corrosion.

VpCI products also have proven useful in protecting electronics. NASA performed extensive testing to address VpCI interference with Hyperbolic Ignition and Lox Mechanical Impact Testing. The products were tested and approved for use.8 Placing the product in enclosed electronic cabinets or boxes allows the inhibitor to form a molecular barrier on the multimetal surfaces of the electrical components. Because the potential adverse effects of molecular layers were of great concern to NASA and the U.S. Navy, extensive testing was conducted that showed VpCI products to be safe for even the most sensitive equipment (i.e., optical coatings and instruments).9 VpCI products effectively and economically protect telecommunication and radar equipment located in highly corrosive environments.

VpCI PROTECTION FOR THE U.S. NAVY

The U.S. Navy uses VpCI-emitting devices for electronics on naval aircraft, ships, and air stations.^{2,10} These products also are used effectively on other sites on naval vessels to combat corrosion caused by continuous exposure to a saltladen environment. In addition, VpCI additives are used in coatings and oils.

VpCI PROTECTION OF WEAPONRY

VpCI products and systems are available in the following forms: film and paper for storage and shipping, lubricating oils, protective coatings, and emitting devices. Each form is a proven, reliable, and effective method for protecting weaponry. Recent testing has been completed on the use of VpCIs in the conservation of infantry weapons in the Armed Forces of the Republic of Croatia.

Degreased and cleaned, unpainted weaponry parts were coated with a thin layer of protective MIL-P-46002B¹¹ VpCI oil, using a brush or brush soaked in oil (Figure 1). The weaponry was then mounted onto special holders and left for 10 to 15 min. so excessive protective oil could drain into previously prepared containers (Figure 2). The oilcoated weaponry was placed into protective MIL-B-22020C12 VpCI bags. The bags were sealed with self-adhesive tape or were welded shut using specialized equipment (Figure 3). The protected weaponry was loaded into crates for warehousing, making sure not to damage the VpCI bags. The weapons were stored in different climates-a mild, Mediterranean climate; a cold, mountain climate; and a dry, continental climate.

After 3 years of storage, the protected weaponry was examined for evidence of corrosion. All metal parts and barrels were in excellent condition—including the weaponry stored near the sea in the presence of a significant concentration of chloride salts and weaponry enclosed in plastic bags that were damaged around the mouth of the barrel and sights. The examination verified the protective effect of VpCIs and extended the conservation period, resulting in significant savings for weaponry protection.

Benefits of VpCI Technology

Through widespread use of VpCI products and systems, military organizations continue to benefit from successful corrosion prevention and the following additional advantages associated with using VpCI technology:

Ease of application

Efficiency in application and nonremoval (removal only if necessary)

- Environmentally friendly
- Economic advantages
 - Low-cost products
 - Reduced labor costs for application and removal
 - Reduced maintenance costs
 - Less-frequent reapplication of products
 - Reduced loss of assets
- Enhanced combat readiness

Extended life expectancy of equipment.

Conclusions

VpCI technology continues to advance as evidenced by expanded utilization and testing of VpCI products and systems by military organizations for preventing corrosion. VpCI use is effective in protecting the safety of military personnel, eliminating hazardous waste disposal, reducing labor costs, and preserving war readiness. The efficiency and ease of application along with the benefit of nonremoval (in most instances) make VpCI technology a desirable alternative for military organizations.

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FIGURE 1



Degreased and cleaned, unpainted weaponry parts coated with VpCl oil.

FIGURE 2



VCI oil draining into previously prepared containers.

FIGURE 3



Weaponry to be packed in VpCI bags

Vapor Phase Corrosion Inhibitors Protect Fire Water Systems

orrosion leads to pinhole leaks in the piping of today's fire sprinkler systems. Such systems include:

■ Wet pipe systems— The most common sys-

tems, these are used in buildings where there is no risk of freezing. Wet systems are required for high-rise buildings and for public safety.¹

Alternative systems—As the name suggests, the pipes of alternative systems can be full of water for the summer and be drained and filled with air under pressure for the winter. Alternative systems are used in buildings that are not heated.¹

■ Dry pipe systems—The pipes in dry pipe systems are filled with air under pressure, and a control valve holds the water back. When a sprinkler head opens, the drop in air pressure opens the valve and water flows into the pipe work and onto the fire. These systems are used where the wet or the alternate systems cannot be used.¹

■ Deluge systems—These are used in special cases for industrial risks (e.g., off-shore oil rigs).

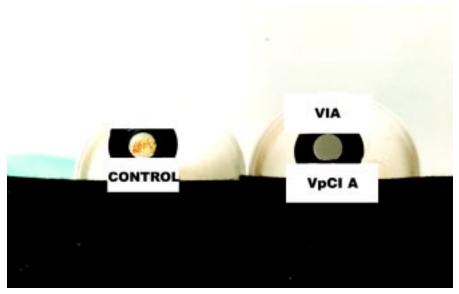
FM Global (Johnston, Rhode Island), a commercial and industrial property insurer, inspected several fire sprinkler systems following reports of leakage visually identified by building owners.² The insurer identified leakage and related encrustation and corrosion that could prevent the sprinklers from operating as designed in the event of a fire. Often, a leak in the fire protection system is the only means of discovering internal corrosion problems.

Underwriters Laboratories, Inc. (UL) (Northbrook, Illinois) recently conducted laboratory tests on dry sprinkler systems taken from field installations. The test results indicated that exposing these sprinkler systems to harsh environmental conditions over an extended period of time may render them inoperable under certain fire conditions.³ In dry

Ashish Gandhi

Corrosion is a problem faced by the fire sprinkler industry in both wet and dry sprinkler system piping. The ability of vapor phase corrosion inhibitors (VpCls) to protect fire water systems was tested in the laboratory and field. The test results show that VpCls provide protection in the conditions present in wet and dry pipe systems.





Vapor Inhibiting Ability test results for steel plugs in VpCI A.

TABLE 1 VIA TEST RESULTS FOR VPCI A

Sample	Results ^(A)
Control	Fail
VpCI A	Pass
•	

^(A)The test procedure contains pictures showing four grades of test results (0 to 3) with varying degrees of corrosion. Zero and 1 "fail"; 2 and 3 "pass."

systems, the problems go undetected until the system fails to perform when needed in the event of a fire or until a system inspection is made.

For a particular treatment program to protect fire sprinkler systems from corrosion effectively, the inhibitor must meet the following criteria:

Prevent corrosion of systems manufactured predominantly from ferrous metals

Prevent corrosion of systems composed of nonferrous alloys

Have a low environmental impactHave low toxicity and skin irritabil-

ity in case of contact with humans.

The corrosion protection properties of vapor phase corrosion inhibitors (VpCIs) were evaluated for dry and wet fire water systems. Laboratory tests were followed by field applications.

VpCI Treatment Programs

Recent VpCI treatment programs based on ambiodic inhibition (i.e., inhibition at the cathodic and anodic sites) have been developed and evaluated in the laboratory. These treatment programs protect ferrous and nonferrous alloys by providing three-phase corrosion protection as follows:

In the water phase

■ In the interphase, between water and air

■ In the air/vapor phase.

VpCIs have been used by automobile manufacturers, the marine industry, and other environmentally sensitive industries to meet stricter environmental regulations. Knowing the mechanism of corrosion protection and the fact that the new generation of VpCIs are safe to use and have a low environmental impact was a good starting point for evaluating the chemicals' effectiveness in protecting fire water systems.

Corrosion and Environmental Laboratory Testing

Two VpCIs—VpCI A and VpCI B were evaluated in the laboratory. VpCI

TABLE 2

FULL-IMMERSED AND HALF-IMMERSED RESULTS FOR VpCI B

Time before corrosion (days) ^(A)		
Metal	Ambient Temperature (°C)	50°C
CS	40+	40+
CS ^(B)	40+	20+
Copper	60+	60+

^(A)Test samples are checked several times a day for onset of corrosion. The sample is considered "failed" at the first sign of corrosion.

^(B)Half-immersed test results.

A, made of amine carboxylates, was examined in corrosion and toxicity tests. It was identified for use in dry and wet systems involving ferrous metals. VpCI B, a blend of amine carboxylates and triazole chemistry, was tested for corrosion protection and skin irritability. (Because VpCI B is based upon chemistry similar to that of VpCI A, costly toxicity studies were not performed on this inhibitor at the time of this study.) VpCI B was identified for use in dry and wet systems involving nonferrous alloys. Although microbiologically induced corrosion (MIC) is one concern in fire water systems, these tests were devoted primarily to general and pitting corrosion. MIC historically has been ad-

In dry systems, the problems go undetected until the system fails to perform when needed in the event of a fire or until a system inspection is made. dressed by using biocides. Biocides are either used to sterilize the systems with shot treatments prior to filling the fire water systems or they are added with the firewater.

CORROSION TESTS

The Vapor Inhibiting Ability (VIA) test method⁴ was used to evaluate VpCI A while the Immersion and Half-Immersion Corrosion test was used with VpCI B.

VIA Test

In the VIA test, the VpCI source never comes in contact with the metal specimen. A freshly polished steel specimen was placed in a 1-L glass jar that contained a measured amount of water blended with glycerin to control the relative humidity. A control sample consisted of a jar containing only a steel specimen, while the test sample comprised the jar with the steel specimen and VpCI A. After a conditioning period during which the VpCI vapors migrated from the source to the metal specimens, the jars were placed in an oven set at 50°C for 4 h. The jars were then placed at ambient temperature and the metal specimens rapidly cooled; this led to condensation from the humid atmosphere. Effective VpCI compounds provide protection in this environment, while the control specimen corrodes heavily. The test samples were run in triplicate. Table 1 presents the results for the VIA test. Following

TABLE 3 BIOACCUMULATION RESULTS (LOG P_{ow}) FOR VpCI A

Test Method	Limit	Result
OECD 117 log P _{ow}	< 3	< 0

TABLE 4 PRIMARY IRRITATION RESPONSE CATEGORIES

Response Category	Comparative Mean Score (PII ^(A))	
Negligible	0 to 0.4	
Slight	0.5 to 1.9	
Moderate	2 to 4.9	
Severe	5 to 8	

^(A)The Primary Irritation Index (PII) is determined by adding the Primary Irritation Score for each animal and dividing the total score by the number of animals.⁷¹⁰

the conditioning period, VpCI A protected the steel specimen in the moisture-condensing environment. Figure 1 shows the appearance of the plugs at the completion of the test.

Immersion and Half-Immersion Corrosion Test

Corrosion tests using VpCI B were performed on immersed and halfimmersed carbon steel (CS) and copper panels at room temperature and at 50° C.⁵ The CS panels were made from cold-rolled steel (ASTM C1010⁶) ground on both sides. The copper (CD A110) panels were sanded with 320grit sandpaper. The panels and working electrodes were washed with methanol (CH₃OH) prior to testing. Table 2 presents the test results.

ENVIRONMENTAL AND SKIN IRRITABILITY TESTS

VpCI A was evaluated in bio-accumulation, biodegradability, and aquatic toxicity tests. VpCI B was used in the skin irritability test, which was designed to determine the dermal irritation potential of the inhibitor on the shaved skin of a rabbit as required by regulation of medical device biocompatibility.

Table 3 presents the results of the bioaccumulation test. With a value of the partition coefficient (P_{ow}) below zero, VpCI A is unlikely to have toxic effects on aquatic life over long time periods. The inhibitor's quick biodegradability, fully decomposing in <28 days, also verifies its limited effect on the marine environment.

Aquatic toxicity results showed that VpCI A is not classified as an acute toxicant to primary producers (algae and aquatic plants), consumers (fish and crustaceans), and sediment reworkers (seabed worms).

Table 4 shows the irritation response categories for the skin irritability test. At a working concentration of 0.4% of VpCI B, the Primary Irritation Index was 0—meaning that the inhibitor falls under a negligible response category for skin irritability.

Case History: Field Corrosion Testing

A large oil and gas producing company that operates several offshore and onshore installations was experiencing serious corrosion problems and nozzle blockages in the deluge fire water system. A unique method, using 5%-bymass VpCI A concentrate solution as a corrosion inhibitor, was developed to solve the company's problem. A 19mm predrilled plug was fitted at the junction where the pipe work terminates. A fogging nozzle connected to compressed air was inserted. Airflow was established and a measured amount of VpCI A concentrate was introduced into the amplified air stream. Wet fog emission through the sprinkler nozzle was verified to ensure proper application. This method of protection with VpCI A decreased blocked nozzles by 97.6% within the first year and 98.8% at the end of 2 years. Using VpCI A dramatically reduced corrosion problems for the operator over the span of 2 to 3 years.

Conclusions

The three-phase protection ability of VpCIs allows them to be effective in the conditions present in dry and wet fire water systems. Corrosion and toxicity testing demonstrated that new VpCIs not only provide excellent corrosion protection but also have low toxicity. Skin irritability testing showed that these compounds are safe for human contact. As environmentally sound, safe, and cost-effective compounds, VpCIs are viable alternatives for protecting fire sprinkler systems from corrosion.

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Environmentally Friendly VCIs

CHRISTOPHE CHANDLER AND BORIS A. MIKSIC, FNACE

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.

> riginally 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.¹⁸ 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.

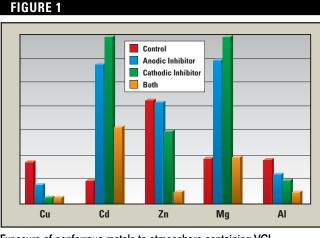
VCIs were originally developed to protect ferrous metals in tropical environments; however, recent developments in VCI chemistry are based on the synthesis of compounds that provide general protection (i.e., they protect most commonly used ferrous and nonferrous metals and alloys) (Figure 1). Electrochemical 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.

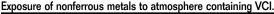
The inhibition mechanism proceeds as follows:

Metal -
$$R_1 - R_0 - R_2$$

:
Metal - $R_1 - R_0 - R_2$
:
Metal - $R_1 - R_0 - R_2$

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





ing the penetration of aggressive ions. As the inhibitor molecules are adsorbed on the metal surface, the R₂ 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.⁹ 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, carbon 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_2O_3) paper at 90 degrees to the previous abraded marks. The plugs were cleaned with methanol (CH₃OH), allowed to air dry, and placed in a dessicator.

Ten mL of a synthetic glycerinwater 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.

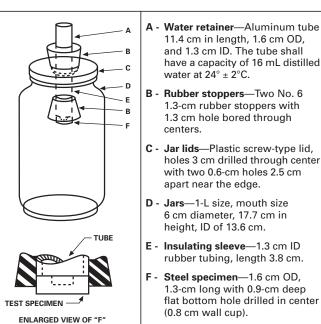
The assembly was exposed to a temperature of 24°C for 20 h. Cold water at a temperature of 4°C below the ambient temperature was added to the aluminum tubes until they were full. After 3 h, the water was removed from the tubes. The steel plugs were evaluated for signs of corrosion. In this test method, 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.

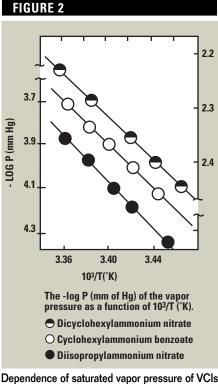
ENVIRONMENTAL TESTING

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





VIA test assembly.



Dependence of saturated vapor pressure of VCIs upon temperature.

TABLE 1

VIA TEST RESULTS

Results
Fail
Pass

FIGURE 4 FIGURE 5 ---- VCI A Sodium benzoate 120 100 80 % 60 40 20 PLUG #1 PLUG #2 PLUG #3 CONTROL 0 VCI A 10 15 20 25 30 Time (Days) VCI A aerobic biodegradability. 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 noctanol/water partition coefficient of a specific chemical compound. In testing the VCI A compound, the partition coefficient Pow 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].¹⁰

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 306,10 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 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 EC₅₀ for an algae species, a 48-h EC₅₀ for a crustacean species, and a 240-h LC_{50} for a sediment reworker. EC₅₀ 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 10253¹¹ (fourth working draft, "Water Quality—Marine Algae Growth Test with *Skeletonema costatum* and *Phaoedactylum tricornutum*) test method

Crustacean test—ISO/DIS 14669-97¹² ("Water Quality—Determination of Acute Lethal Toxicity to Marine Copepods") test method

■ Sediment reworker test—ASTM E1367-90¹³ ("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,¹⁰ the upper limit for acute toxicity measured as 72-h EC₅₀ is 100 mg/L in the case of algae or other aquatic plants. The test results show that the 72-h EC₅₀ 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 ₅₀	72	240	≥100
$EC_{50} EC_{90}$	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 ₅₀	48	100	≥100
	48	220	_
LC ₅₀ LC ₉₀ 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^3 . 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-

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.

TABLE 5

Concentration

LC₉₀ No observed effect

concentration

LC₅₀

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

$$Q = 0.0277VC$$

Where Q = total quantityof VCI powder, oz; V = volume of the enclosure to be protected, ft^3 ; and C = confidence factor (2 to 3). The cost per unit of volume per year is nominally \$0.01 per ft³.

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 A TOXICITY TO SEDIMENT REWORKERS

Exposure

. Time (h)

240

240

240

(1)

VCI Performance in Industrial and Marine Atmospheres

Limit (mg/L)

≥100

 All corro	sion rates	in mi	Is/v

Effect

Concentration (mg/kg)

1,410

2,800

1,014

Aluminum			
(1000, 300, 5000			
6000 series)		2.15	<0.25
Mild Steel		21.8	<0.13
HSLA (high-stren	ath	21.0	10.10
low-allov steel		1.2	0.08
Naval Brass		0.2(B)	0.03
Titanium		0.0(C)	0.0(C)
Stainless Steels: 410	410	0.01(D)	0.01(E)
	304	<0.1 ^(F)	0.01(G)
	301, 316,		0.01
	and 321	0.0 (H)	0.0 (H)
Copper		0.22 ^(F)	0.01 ^(G)
Notes:			
	lation (B)	Desingification (C) Immune to attack:

VCI performance in industrial and marine atmospheres.



Metering station.



Onshore pipeline 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-ft³ (0.03- to 1.13-m³) 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:

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.

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

Where N = numberof devices needed to protect a given volume under specific conditions; $k_a = factor ex$ pressing the corrosiveness of the environment; $k_p = factor ex$ pressing frequency of opening or breathability of the enclosure; $k_s = factor expressing$ the shape of the enclosure; and N_0 = 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.

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