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MATERIALS PERFORMANCE
CORROSION PREVENTION AND CONTROL WORLDWIDE

PROTECTING LARGE-VOLUME STORAGE SYSTEMS WITH A FLOAT COAT

High-Performance Coatings for Corrosion Control

Cathodic Protection Interactions with a Vapor Phase Corrosion Inhibitor

Impact of VCI Particle Size on Corrosion Inhibiting Effectiveness

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SUPPLEMENT TO **JUNE 2017**

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CORROSION PREVENTION AND CONTROL WORLDWIDE

MATERIALS PERFORMANCE

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VAPOR PHASE CORROSION INHIBITORS

PROTECTIVE COATINGS

Economic, Environmentally Friendly Solutions for Corrosion Prevention and Control

Vapor phase corrosion inhibitors (VCIs) have been used for many years to protect structures, equipment, and the environment from the adverse effects of corrosion. These technologies offer a variety of benefits, including easy, economical application and earth-friendly qualities. This special supplement to *Materials Performance* magazine describes several projects where VCIs have been effectively used, including applications for protecting the bottoms of aboveground storage tanks and the impact of powder particle size on corrosion inhibiting effectiveness. Articles on protective coatings and VCIs describe a high-performance water-based coating and the use of a float coat for petrochemical storage systems. Whether asset preservation is a matter of product containment or keeping structures safe and intact, environmentally friendly VCIs are proven to control corrosion in a multitude of applications.

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NACE International Contact Information

Tel: +1 281-228-6200 Fax: +1 281-228-6300
Email: Firstservice@nace.org Web site: nace.org

Influence of Powder Size of the Vapor Corrosion Inhibitor on Inhibiting Effectiveness

Behzad Bavarian, Lisa Reiner, and Babak Samimi, *California State University Northridge, California, USA*
Boris A. Miksic, FNACE, *Cortec Corp., St. Paul, Minnesota, USA*

The protection effectiveness of commercially available vapor corrosion inhibitor powders with different particle sizes was evaluated. Conventional powder size of nanoparticle powder inhibiting effectiveness was compared using a vapor-inhibiting ability (VIA) test method. Optical microscopy post VIA corrosion tests revealed that the particle size of inhibitor powder has a significant influence on the degree of protection. The nanoparticle inhibitor showed a corrosion rating of Grade 4 and >41% decrease on the corrosion rate both in electrochemical tests and continuous exposure tests compared with the inhibitor with coarse particle size. Surface coverage also showed improvement mainly due to an increase of effective surface area and the partial pressure of vapor inhibitors as powder particle size decreased. Adsorption energy was roughly –16,740 J/mol for the nanoparticle-size inhibitor, while adsorption energy was roughly –13,660 J/mol for the coarse-particle-size inhibitor. This was indicative of a stronger physical adsorption to the metal surface for the nanoparticle than the coarse inhibitor, leading to better corrosion protection. Laser Doppler anemometry measurement using the Doppler shift in a laser beam to measure the flow velocity showed a velocity of 6 ft/s for the nanoparticle and uniform flow. The coarse-particle inhibitor had a lower velocity of 3 to 4 ft/s and nonuniform flow.

Corrosion inhibitors can adsorb to a metal surface, protecting it from the environment by forming a nonreactive, hydrophobic layer that prevents corrosion. To be effective, an inhibitor will interact with the anodic or cathodic sites to slow oxidation and reduction reactions. Vapor phase corrosion inhibitors (VCIs) rely on vapor pressure for transport of active inhibitor compounds. VCIs form a bond with the metal surface and create a barrier layer to minimize corrosive ions on the surface. VCIs can be used alone or incorporated into packaging materials, oils, chemicals, and coatings. Some applications have been demonstrated for long-term (two years or more) storage of liquefied natural gas piping in Abu Dhabi, United Arab Emirates; power and desalination plant boiler tubes, also in Abu Dhabi; and gas pipe flanges in Wales, United Kingdom.[1] Other applications include aboveground storage tanks with underside corrosion between the tank bottom plate and its concrete foundation.[2]

The mechanism of the nanoparticle VCIs involves the transport of the inhibitor to the metal surface and the inhibitor interaction with the metal substrate to form a protective film. When added to a liquid coating, the inhibitors react with water and dissociate. After application, as the liquid coating cures, the charged inhibitors migrate and adsorb onto the bare metal surface. Adsorption occurs as a result of electrostatic forces between the electric charge of the metal and the ionic charges of 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.[3-5] A good level of corrosion protection can be obtained with an inhibitor that forms a passive microphobic layer on the metal surface using micron-size powder particles. However, as a result of the larger particle size, gaps may exist between the particles that are deposited on to the metal surface. This lack of coverage provides an opening for corrosive species to attack the unprotected surface (Figure 1).

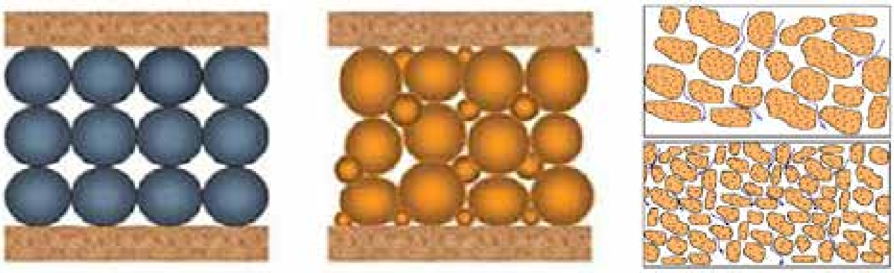

FIGURE 1 Particle size variation can lead to ingress of corrosive species that may attack the surface of the metal.

Particle size influences many properties and is a valuable indicator of performance. This is true for powders, suspensions, emulsions, and aerosols. The size and shape of powders influences flow and compaction properties. Larger, more spherical particles will typically flow more easily than smaller particles that tend to agglomerate.[6] Smaller particles dissolve more quickly and lead to higher suspension viscosities than larger ones. In the case of a VCI, size also matters.

Figure 2 shows a comparison of particles, contaminants, and the agglomeration of small particles, all of which can influence the effectiveness of corrosion protection. Nanotechnology deals with structures that are 100 nm or smaller and involves developing materials or devices within that size range. To improve corrosion performance, nano-size powders are incorporated into VCIs. Particle deposition is the spontaneous attachment of particles to surfaces. The particles in question are normally colloidal, while the surfaces involved may be planar, curved, or represent particles much larger in size than the depositing ones. Depositing particles may form a monolayer that inhibits further particle deposition or may facilitate further particle deposition depending on the dynamics.

As determined in this research, the VCIs are adsorbed to the metal surface by physiosorption. Irving Langmuir developed an adsorption isotherm that models gases adsorbed to solid surfaces.[7-10] It is a semi-empirical isotherm with a kinetic basis and was derived based on statistical thermodynamics. It is the most common isotherm equation to use due to its simplicity and its ability to fit a variety of adsorption data. It is based on four assumptions:

1. All of the adsorption sites are equivalent and each site can only accommodate one molecule.
2. The surface is energetically homogeneous and adsorbed molecules do not interact.
3. There are no phase transitions.
4. At the maximum adsorption, only a monolayer is formed. Adsorption only occurs on localized sites on the surface, not with other adsorbates.

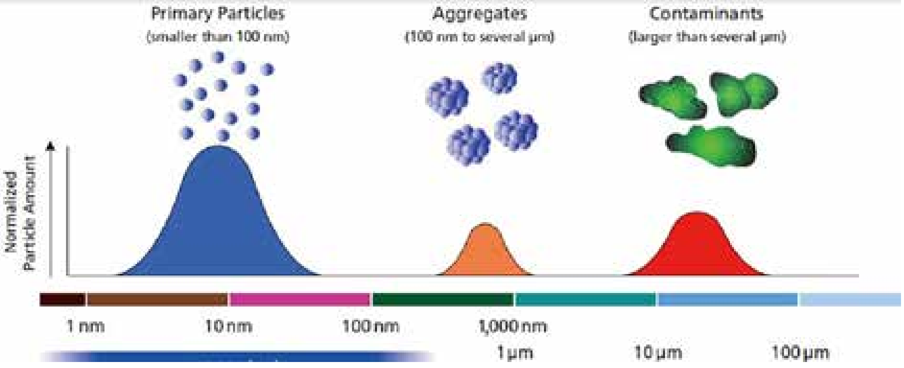

FIGURE 2 Relative size for particles, aggregates, and corrosive species.

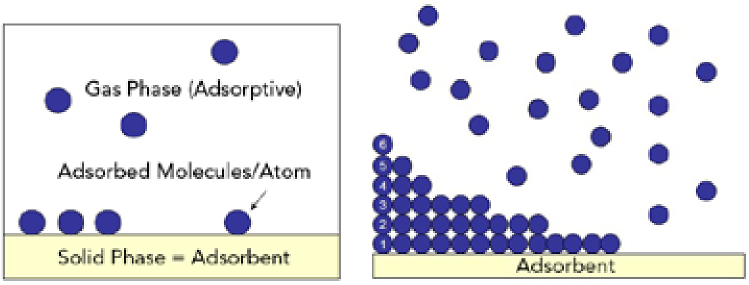

FIGURE 3 Atomic models for possible types of surface coverage, monolayer or multiple particle deposition on the metal.[11]

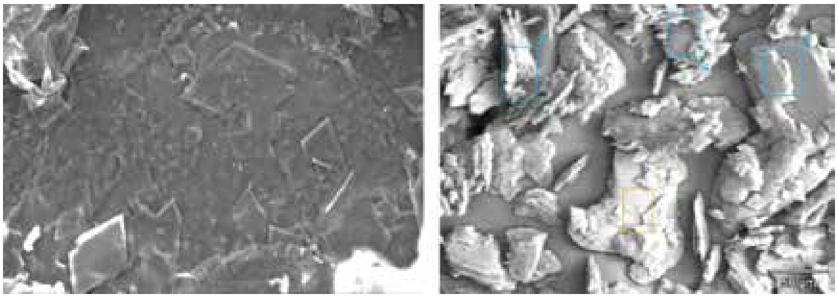

FIGURE 4 Left: VCI-A nano-size particle. Right: VCI-A coarse particle.

Some of the criteria assumed in Langmuir's model do not fit with the observations from this investigation. There are always imperfections on the surface, adsorbed molecules are not necessarily inert, and the mechanism is clearly not the same for the first molecules to adsorb to a surface as for the last molecules. Another condition has to do with the thickness of particle deposition, and more likely, molecules will adsorb to the initial monolayer. Despite its shortcomings, the Langmuir isotherm has many applications in surface kinetics. For the Brunauer Emmett Teller (BET) Model (an isotherm developed by Stephen Brunauer, Paul Emmett, and Edward Teller), given that the four assumptions made to fit the Langmuir isotherm model are, in general, not realistic, it is assumed that the molecules may form multilayers (Figure 3). However, BET theory ignores inhomogeneities of the surface and lateral adsorbate-adsorbate interactions.[11]

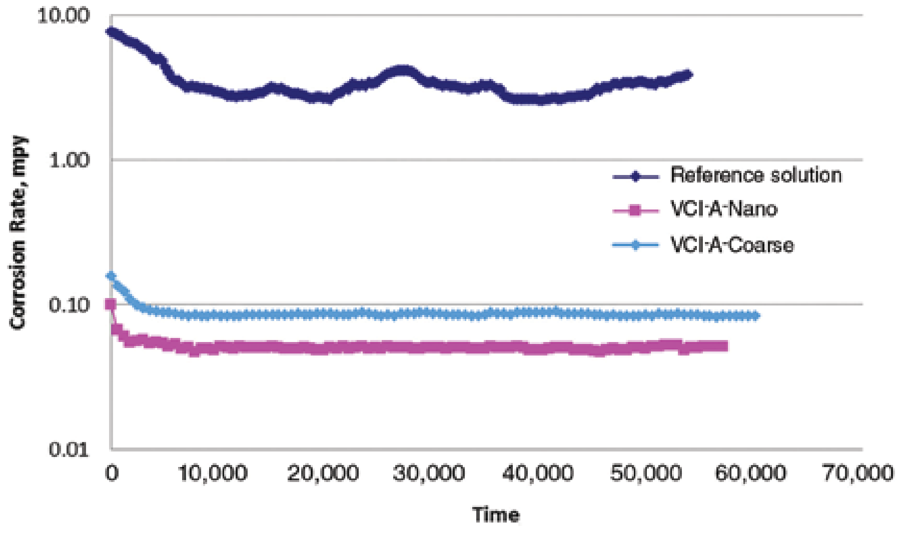

FIGURE 5 Comparison of corrosion behavior of different particle sizes for VCI-A in 200 ppm chloride solution for UNS G10180 steel.

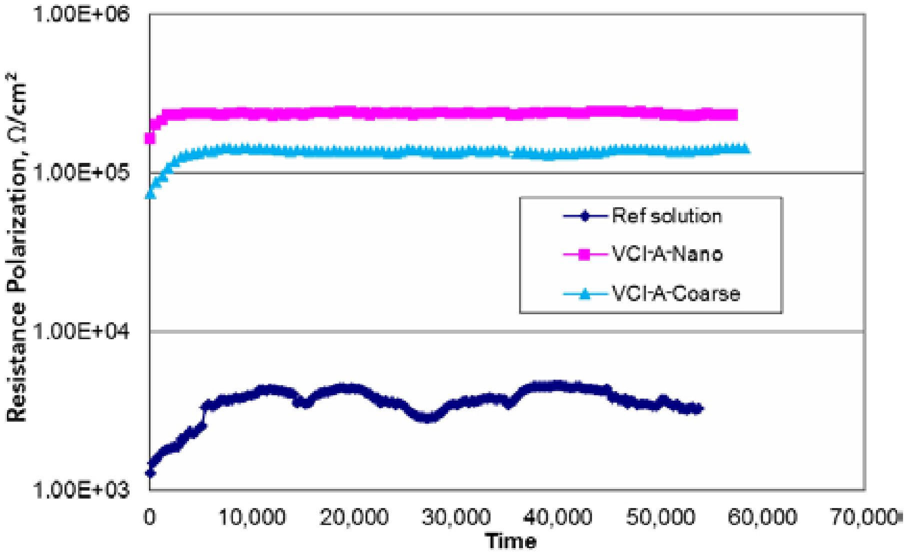

FIGURE 6 Comparison of polarization resistance for different particle sizes of VCI-A in 200 ppm chloride solution for UNS G10180 steel.

Experimental Procedure

Corrosion behavior of carbon steel (CS) (UNS G10180) samples were studied in two different VCIs with coarse particles (~150 µm, VCI-A-Coarse) and those with nanoparticles (~500 nm, VCI-A-Nano) using NACE International TM0208-2013.[12-13] Figure 4 shows the difference in particle size for these two inhibitors. This laboratory test method evaluates the vapor-inhibiting ability (VIA) of various forms of VCI materials for temporary corrosion protection of ferrous metal surfaces. The VIA corrosion test method provides for standard conditions in a test jar of water-saturated warm air without the presence of accelerating contaminants. Water vapor and VCI transport are confirmed and corrosion protection is evaluated in this test method. The VIA tests consist of four steps of sample conditioning or saturation for 20 h at 22 °C, cooling cycle at 2 °C, and prewarming at 50 °C, followed by 3 h at 22 °C for specimen conditioning. After the last 3-h conditioning period, the steel samples were inspected for visible water condensation. Following verification of water condensation on each sample, visual examination of the surface was done and microscopic observation was conducted to determine the corrosion rating for each sample. The corrosion criteria for rating steel specimens consist of Grade 0 through Grade 4. To have a valid test, the control sample must have Grade 0; samples with no inhibitor received the worst grade. The control samples consistently rated a Grade 0 for all VIA tests, therefore validating the test method. Relative humidity and the temperature of each test jar were monitored by Sensirion[†] sensors and data logging software.

Electrochemical polarization standards for corrosion rate and resistance polarization (Rp/CR) measurements using Gamry Rp/CR[†] techniques were also used to evaluate the behavior of this inhibitor on the steel samples in 200 ppm chloride solution and to compare overall corrosion behavior of these different particle size corrosion inhibitors. These electrochemical tests were conducted using Gamry PC4/750 Potentiostat/Galvanostat/ZRA[†] instrumentation and DC105[†] corrosion test software. Samples were polished (1.0 µm), placed in a flat cell, and tested in deionized water solutions containing 200 ppm Cl- and 0.5% and 1.0% VCI.

Corrosion tests also were conducted by exposing the CS samples to the misted sand with and without inhibitor to simulate similar condition of the aboveground storage tanks bottoms. Test duration was 120 d while the sand was misted by 200 ppm chloride solution every 72 h. Corrosion rates were monitored using electrical resistance probes.

Samples were visually inspected and their surface conditions were documented after VIA tests were completed. Photography, optical microscopy, and scanning electron microscopy/energy-dispersive x-ray spectroscopy (SEM/EDXS) analysis were

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[†] Trade name.

conducted using a JEOL JSM-6480LV† and Thermo System Seven detector.†

Electrochemical polarization test results for the polarization resistance and corrosion rate measurements are shown in Figures 5 and 6. Both corrosion rate and polarization resistance data showed that VCI-A nano-particles have a 41% lower corrosion rate compared with the coarse-particle size. The VIA visual observations are shown in Figure 7. The corrosion rating per NACE TM0208 indicated that the control sample had Grade 0, while the VCI-A coarse-particle rating was Grade 2, and VCI-A nanoparticle rating was Grade 4. The surface condition of samples after VIA tests is shown in Figures 8 and 9. The VCI-A nanoparticle tested samples showed superior corrosion protection during VIA tests. Figures 10 and 11 show significant reduction of the corrosion rate of UNS G10180 steel, continuously exposed (120 days above mist sand corrosion tests, 200 ppm Cl- solution added to sand bed every 72 h) when inhibitor was added to the environment.

The adsorption isotherm relationship between surface coverage and temperature for both VCI-A-Coarse and VCI-A-Nano inhibitors on the surface of steel is shown in Figure 12. Adsorption energy was roughly –16,740 J/mol for the nanoparticle-size inhibitor, while adsorption energy was roughly –13,660 J/mol for the coarse-particle-size inhibitor. This energy range is indicative of a strong physical adsorption to the metal surface.[14] However, it can be seen that the interaction of VCI-A-Nano with the steel surface is higher than the coarse inhibitor, leading to better corrosion protection. The size effect of this inhibitor appears to be more pronounced at higher temperature than the room temperature. X-ray photoelectron spectroscopy (XPS) depth profiling analysis showed ~60 to 80 nm of adsorbed inhibitor on the exposed samples, indicating that the multilayer BET Model is a more realistic adsorption model than the monolayer Langmuir model for this case. But for the adhesion energy calculation between inhibitor molecules and metal surface, it is appropriate to use the monolayer Langmuir model.

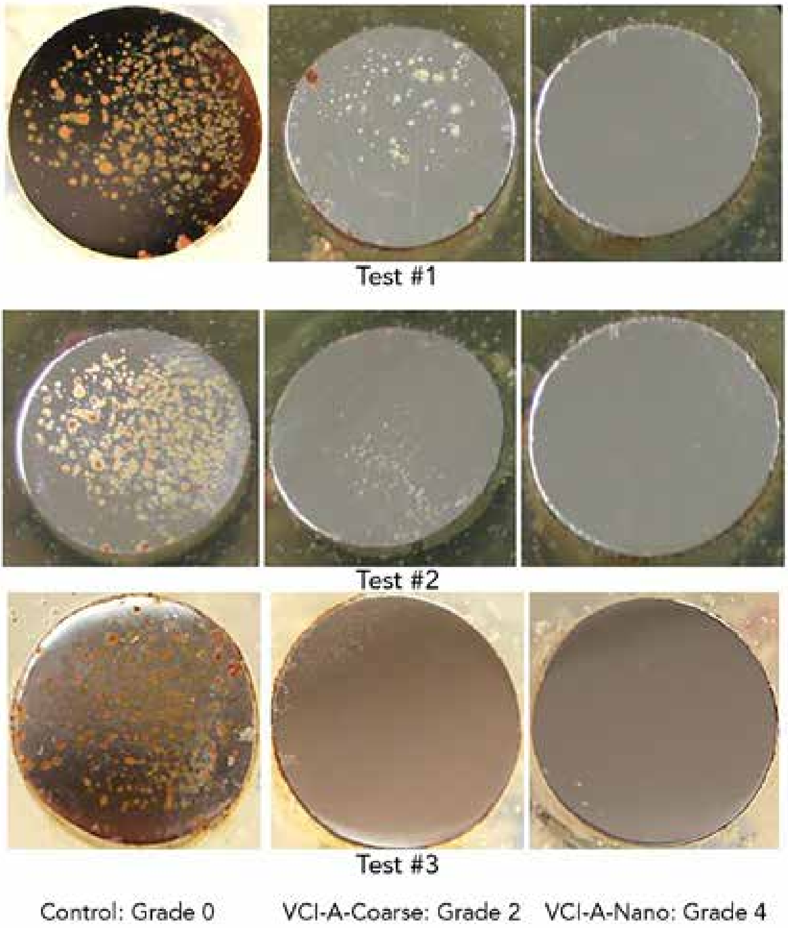

FIGURE 7 Photographs of steel samples after VIA tests and their corrosion rating; shows superior performance for VCI-A-nano exposed samples.

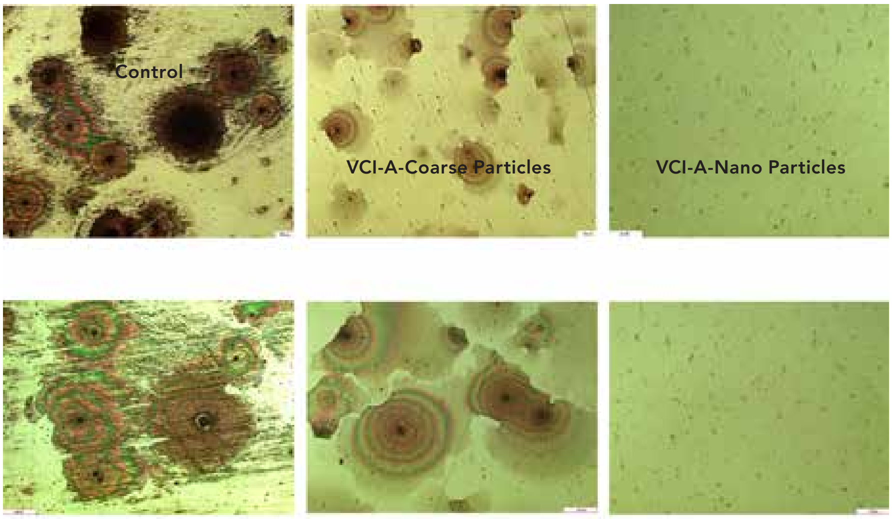

FIGURE 8 Optical micrographs of steel samples after VIA tests; superior performance is seen for VCI-A-Nano exposed samples.

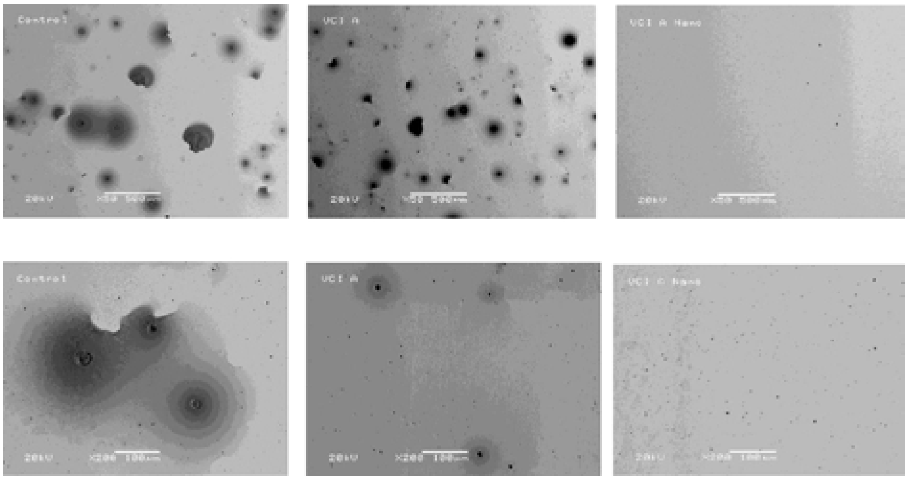

FIGURE 9 SEM micrographs of steel sample after VIA tests. Superior performance for VCI-A nano exposed samples. The black dots on the VCI-A nano samples are mainly alloy inclusions.

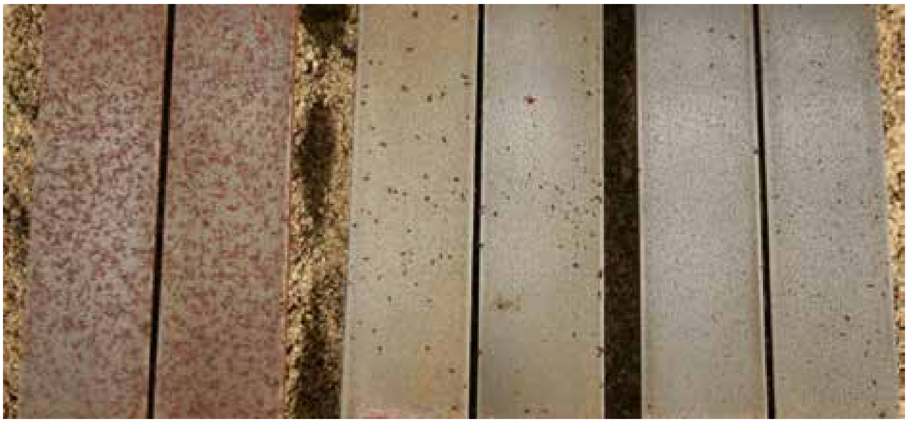

FIGURE 10 Comparison of corrosion behavior of UNS G10180 steel, continuous exposure (120 days above mist sand corrosion tests, 200 ppm Cl- solution added to sand bed every 72 h).

Conclusions

The effectiveness of commercially available VCI powders with different particle size was evaluated. Conventional powder size and nanoparticle powder inhibiting effectiveness was compared. Optical microscopy post VIA corrosion tests revealed that the particle size of inhibitor powder has a significant influence on the degree of protection. The nanoparticle inhibitor showed a corrosion rating of Grade 4 and >41% decrease on the corrosion rate. Surface coverage also appeared to improve, mainly due to the increase of effective surface area and the partial pressure of VCIs as powder particle size is reduced. Adsorption energy was roughly –16,740 J/mol for the nanoparticle size inhibitor, while adsorption energy was roughly –13,660 J/mol for the coarse-particle-size inhibitor, indicative of a strong physical adsorption to the metal surface for both inhibitors. But VCI-A-Nano showed a stronger interaction with the steel surface than the coarse inhibitor, leading to better corrosion protection. Continuous exposure in mist sand corrosion tests verified the corrosion rate reduction by a factor of 10. The laser Doppler anemometry measurement using the Doppler shift in a laser beam to measure the flow velocity showed a velocity of 6 ft/s for the nanoparticle inhibitor and uniform flow, while the coarse-particle inhibitor had a lower velocity of 3 to 4 ft/s and nonuniform flow.

References

1. B.A. Miksic, *Preservation, Lay-up and Mothballing Handbook*, 3rd ed. (St. Paul, MN: Cortec Corp., 2014).
2. M. Kharshan, C. Cracauer, "Applications for Biodegradable Vapor Phase Corrosion Inhibitors," *MP* 50, 3 (2011).
3. B.A. Miksic, M. Kharshan, R. Camp, "Water-Based Coatings Powered by Nanoparticle Vapor Corrosion Inhibitors," *MP* 54, 6 (2015).
4. B.A. Miksic, R.H. Miller, "Fundamental Principals of Corrosion Protection with Vapor Phase Inhibitors," 5th European Symposium on Corrosion Inhibitors, Italy, 1980.
5. J. Holden, A. Hansen, A. Furman, R. Kharshan, E. Austin, "Vapor Corrosion inhibitors in Hydro-testing and Long Term Storage Applications," CORROSION 2010, paper no. 10405 (Houston, TX: NACE International, 2010).
6. Z. Li, C. Zhang, J. Zhu, "Numerical Study of the Effect of Particle Size on the Coating Efficiency and Uniformity of an Electrostatic Powder Coating Process," *The Canadian J. of Chemical Engineering* 83, 10 (2005).
7. L. Czepirski, M.R. Balys, E. Komorowska-Czepirska, "Some Generalization of Langmuir Adsorption Isotherm," *Internet J. of Chemistry* 14, 3 (2000).
8. M. Lagrenée, B. Mernari, M. Bouanis, M. Traisnel, F. Bentiss, "Study of the Mechanism and Inhibiting Efficiency of 3,5-bis(4-methylthiophenyl)-4H-1,2,4-triazole on Mild Steel Corrosion in Acidic Media," *Corr. Sci.* 44, 3 (2002).
9. B. Bavarian, Y. Ikder, B. Samimi, L. Reiner, B.A. Miksic, "Implementation of Vapor Corrosion Inhibitors to Improve Corrosion Protection Effectiveness of Dry Air System," Eurocorr 2015, Graz, Austria, Sept. 2015.
10. B. Bavarian, L. Reiner, H. Youssefpour, "Vapor Phase Inhibitors to Extend the Life of Aging Aircraft," CORROSION 2005, paper no. 05329 (Houston, TX: NACE 2005).
11. A. Trunschke, *Surface Area and Pore Size Determination; Modern Methods in Heterogeneous Catalysis Research* (2007).
12. NACE TM0208-2013, "Standard Test Method Laboratory Test to Evaluate the Vapor-Inhibiting Ability of Volatile Corrosion Inhibitor Materials for Temporary Protection of

Ferrous Metal Surfaces" (Houston, TX: NACE, 2013).

13. C. Kraemer, "A Procedure for Testing the Effect of Vapor Phase Corrosion Inhibitors on Combined Multi Metals," CORROSION/97, paper no. 178 (Houston, TX: NACE, 1997).

14. B. Bavarian, J. Zhang, L. Reiner, B.A. Miksic, "Comparison of the Corrosion Protection Effectiveness of Vapor Corrosion Inhibitor and Nitrogen Blanketing System," 16th Nordic Corrosion Congress, Stavanger, Norway, May 2015.

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BEHZAD BAVARIAN is a professor in the Department of Manufacturing Systems Engineering and Management and director of the W.M. Keck Advanced Materials Laboratory at California State University Northridge (CSUN), Northridge, California, USA, email: Bavarian@csun.edu. He received his Ph.D. in metallurgical engineering at The Ohio State University in 1980. He has been a member of NACE International for 34 years and received a 2012 NACE Technical Achievement Award for contributions to corrosion and corrosion engineering.

LISA REINER is a professor in the Department of Manufacturing Systems Engineering and Management and manager of the W.M. Keck Advanced Materials Laboratory at CSUN.

BABAK SAMIMI is a materials and process engineer at MATECH GSM, Westlake Village, California, USA, email: babsamimi@gmail.com. He has an M.S. degree in materials science & engineering from CSUN. His experience involves corrosion and corrosion protection of materials, materials characterization and failure analysis, chemical vapor deposition, and FEA and simulation of high-temperature composites.

BORIS A. MIKSIC, FNACE, is president and chief executive of Cortec Corp., St. Paul, Minnesota, USA. He has served in this capacity for 40 years. Cortec is a world leader in the manufacture of corrosion inhibitors in several industries, including modern plastic products. Miksic holds more than 43 U.S. and foreign patents and patent applications and has presented papers throughout the world. He received the NACE International F.N. Speller Award for longtime contributions to corrosion engineering. A NACE Fellow, he has been a NACE member for more than 40 years. *MP*

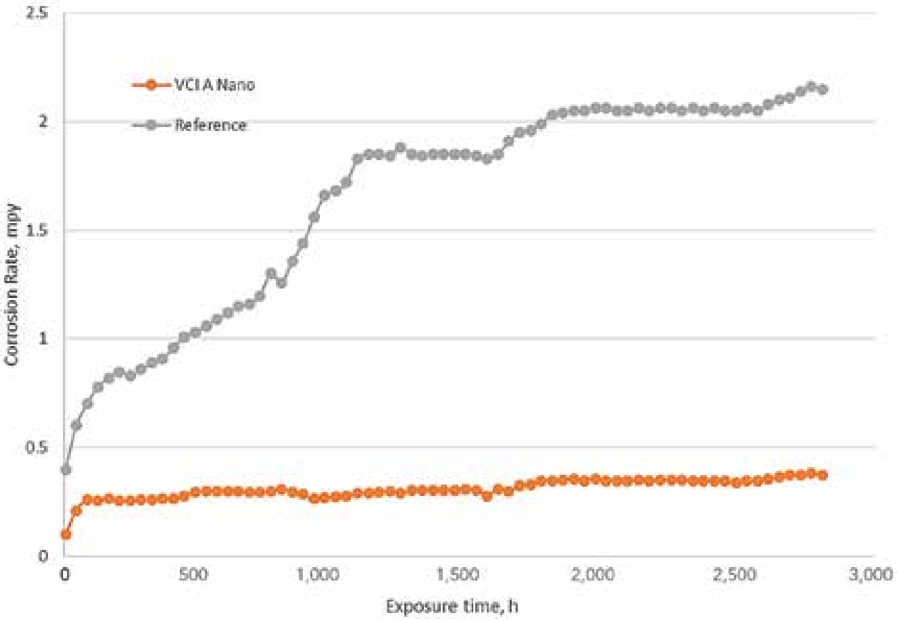

FIGURE 11 Comparison of corrosion behavior of UNS G10180 steel during continuous exposure (120 d above mist sand corrosion tests, 200 ppm Cl- solution added to sand bed every 72 h).

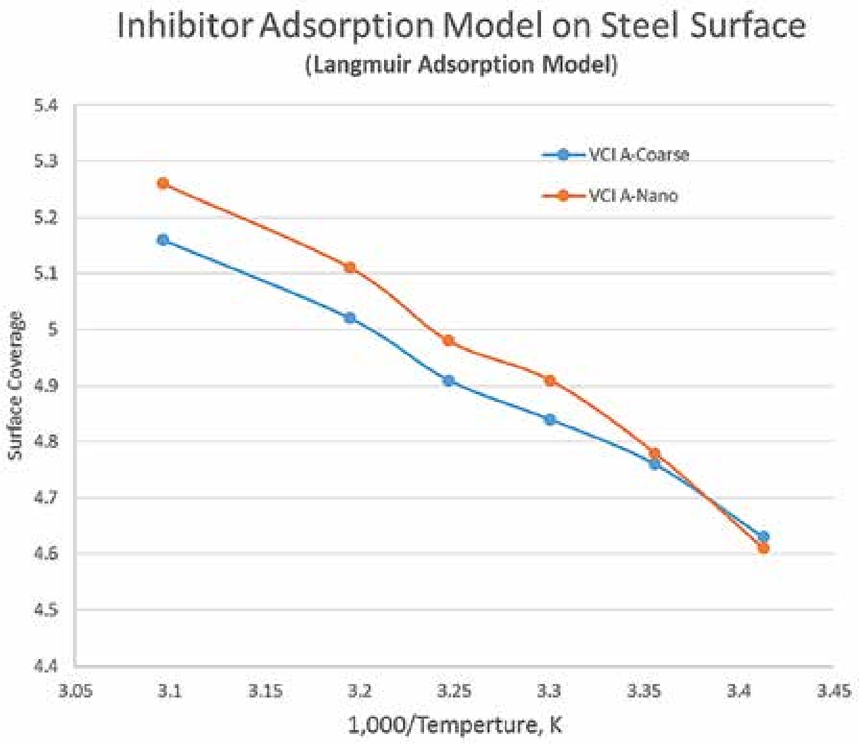

FIGURE 12 The adsorption isotherm relationship between surface coverage and temperature for VCI on the surface of steel.

Using a Float Coat for Preservation of Large-Volume Storage Systems

John Wulterkens and Casey Heurung, *Cortec Corp., St. Paul, Minnesota, USA*
Houssam Sabry, *ADGAS, Abu Dhabi, United Arab Emirates*

Traditional water treatment methods pose several challenges to large-vessel preservation. The economics of continuous dosing and environmental restrictions concerning the disposal of treated water need to be considered. One solution to these challenges involves the application of an immiscible corrosion inhibiting oil partition on the water surface (henceforth referred to as a "float coat"). This article highlights the challenges of traditional preservation methods and examines the efficacy of one commercial float coat. Large vessel preservation is typically accomplished through one of two methods: chemical treatment of water during hydrotesting or heavy-duty epoxy coating systems. These treatment systems have proven to be effective. However, novel approaches to large vessel preservation provide an opportunity to overcome challenges involved with more traditional preservation methods.

There are various water treatment methods available to protect large storage vessels from corrosion, including those used in the petroleum industry. This article describes common methods and presents testing information and conclusions about a coating technology that is cost-effective, environmentally friendly, and suitable for large vessel protection.

Preservation Methods

Chemical Treatment

Aboveground storage tanks (ASTs) in the petroleum industry come in a wide variety of sizes, ranging from modest sizes of 200 m^3 up to storage volumes in excess of 100,000 m^3.[1] For even the most modest dosage rates of chemical treatment at 500 ppm, costs can exceed $2.5 million USD for more than 115 m^3 of chemical treatment.

Coatings

Coatings can be separated into removable, or "temporary" coatings, and permanent coatings. After the application of either type of coating, the proper amount of cure time must be allowed for the coating to achieve peak performance. Typical recommendations call for one week of cure time. During this time, no maintenance or testing can be performed on coated areas, resulting in lost time and productivity.

For tanks with a 91.4-m diameter and 18.3-m wall height,[1] the total wall surface area is approximately 5,300 m^2. Given a spread rate of 3.7 m^2 per liter, over 1,500 L of the coating are required, costing upwards of $40,000. While removable or temporary coatings typically cost less than permanent coatings, the reapplication of any coating for long-term preservation would require significant labor cost for surface preparation and application. Finally, lost time (for product application and cure time) is also a considerable factor, resulting in lost profits.

Waste Disposal

Waste disposal and environmental concerns can be very large factors in determining the efficacy of any procedure whose processes produce any amount of potentially hazardous chemical waste. The cost to properly dispose of "dirty water waste" ranges from $0.04 to $0.24 per cubic m^3.[2] Given a tank size of 100,000 m^3, waste disposal can add up to $24,000 onto existing project costs. Though more modest-sized containers would significantly reduce the cost for waste disposal, this expense still remains a major consideration in the efficacy of any given treatment.

Application of a Float Coat

A float coat is a corrosion-inhibiting oil that is applied to a large-volume system during a typical hydrotesting process. The float coat, being a hydrocarbon-based product, floats on the surface of the water, allowing for a unique application using a much smaller volume of product than typical chemical additives.

The vessel floor and initial meter of wall height is sprayed with a layer of the float coat before any water is added to the system. Water is slowly added, until a point just below the initial spray treatment, so to avoid disturbing the applied float coat protective coating. The remainder of the float coat is applied to the top of the water layer. Hydrotesting is then carried out as normal with care to fill the system at such a rate that the float coat layer on the water's surface is not disturbed. As the hydrotest proceeds, the walls of the vessel are coated with the float coat and further recoated as the vessel is drained.

Experimental Procedures

Using a float coat has proven to be a viable preservation technique for ASTs and other large vessels during hydrotesting via a number of laboratory studies as well as real-life application.

Laboratory Testing: Humidity Testing

ASTM D1735[3] and D1748[4] conditions are standard accelerated weathering environments. Both of these environments were used to evaluate the corrosion resistance of the oil film in non-submerged situations such as the conditions experienced within an AST after a hydrotest and during preservation.

ASTM D1735

ASTM D1735 is a test that examines a coating's resistance to constant water fog in a warm environment. The temperature of the chamber is held at 38 °C (100 °F), and deionized (DI) water is continuously fogged into this space such that 1.0 to 3.0 mL is collected on an 80 cm^2 surface area every hour. Steel panels are cleaned, coated with the float coat, and drained prior to being placed in the test chamber 15 degrees from vertical. Significant corrosion is typically witnessed on control samples within one day, but the duration of testing is dependent on how long the test panels remain free of corrosion.

ASTM D1748

ASTM D1748 is a humidity test that examines a coating's resistance to high temperature and humidity. The temperature of the chamber is held at 48.9 ± 1.1 °C (120 ± 2 °F), and the panels are suspended by hangers designed so water does not drain from the hanger to the panel's surface. These hanging panels are then rotated through the chamber to allow every panel to experience identical conditions. Corrosion is typically witnessed on control samples within one hour, but the duration of testing is dependent on how long the test panels remain free of corrosion. This test was modified by using 0.063- by 2- by 4-in (1.6- by 51- by 102-mm) SAE 1008 cold-rolled steel panels and preparing the surface according to the procedure described in 8.2 through 8.3.6 without performing the heated solvent cleaning described in 8.3.7 through 9.2. Rather, the top edges of the panels were protected after removal from the solvent referenced in Section 8.3.6 and the float coat was applied to the panel as described in Section 9.2.

Laboratory Testing: Immersion Testing

Immersion testing was performed in a 3.5 wt% solution of sodium chloride (NaCl) in DI water. This solution was held in a cylindrical glass cell with a 5-in (127-mm) height and 2-in diameter. Two hundred grams of this solution were used in each test cell to ensure the full immersion of the tested steel panels (0.063- by 1- by 3-in [1.6- by 25- by 76-mm] SAE 1008 cold-rolled steel). Ten grams of preservative oil were added to each cell to build a substantially thick layer on the surface of the water. Pre-weighed steel panels were slowly lowered through the float coat into the test solution to ensure an even coating. These cells were placed into a 40 ± 2 °C oven for two weeks before being removed and left at ambient conditions (22 ± 2 °C) for 21 weeks. At this time the panels were removed, the oil residue was cleaned off with methanol, and oxides were cleaned from the surface via a 7.8 M hydrochloric acid (HCl) solution. The panels were examined for mass loss and the rate of corrosion was calculated using the following formula from ASTM G31[5] (Equation 2, Section 12.4) shown in Equation (1):

$$\text{Corrosion Rate (mpy)} = \frac{3.45 \times 10^6 \times W}{A \times T \times D} \qquad (1)$$

where W represents the mass loss in grams, A is the panel surface area in cm^2, T is the duration of the test in hours, and D is the metal density in grams per cubic centimeter (7.87 g/cm^3 for SAE 1008 steel). The corrosion rate reduction was also calculated by comparing the control sample to the test samples, as shown in Equation (2):

$$\text{Corrosion Rate Reduction} = 1 - \frac{R}{C} \times 100\% \qquad (2)$$

where C represents the corrosion rate of the control sample and R is the corrosion rate of the test sample.

Laboratory Testing: Coating Thickness and Dosing Estimation

Coating thickness and appropriate dosage were determined by constructing a vessel in which to simulate the float coating process. A 5-gal (19-L) container was fitted with a ball valve near its base to act as a drain while a rubber hose, guided to the base of the container via a 1-in diameter polyvinyl chloride pipe, was used to siphon water from another 5-gal container. Four- by twelve-in (102- by 305-mm) SAE 1008 steel panels were suspended in the center of the vessel to act as stationary steel surfaces would in an actual application. The proper dosage was determined by considering the water surface area, monitoring the addition of oil until a consistent film formed on the water, and raising the water level to coat the suspended steel panels. When the coating applied evenly without breaking the oil surface as it was raised over the panel, the dosage was considered adequate for float coat application. After draining the water from the vessel and allowing excess oil to drip from the test panel's surface, the film thickness was evaluated with a standard wet film thickness (WFT) gauge.

Real World Analysis

Float coating has been successfully used as an AST preservation method in the Middle East. This project provided affordable corrosion protection through the application of a float coat while hydrotesting the system. The float coat was applied with neither minimal disruption to normal application procedures nor any negative impact on any cured phenolic epoxy liners, typically used in tanks.

A water sample from the float coat system was submitted to a third-party chemical analysis firm for chemical testing. Analysis for several hazardous chemicals was performed, including dissolved metals, such as lead, mercury, and zinc, and several hazardous hydrocarbons, such as benzene, toluene, naphthalene, and others. Tests were carried out according to APHA 3120 B,[6] U.S. EPA SW 846/8260B,[7] and U.S. EPA SW 846/8081B[8] for various metals, volatile organic compounds, and organochlorine pesticides, respectively. Upon gaining disposal approval, hydrotest water was disposed of with minimal impact to normal operational procedures.

Results

Laboratory Testing: Humidity Testing

ASTM D1735

Product A was tested according to ASTM D1735 to assess its corrosion protec-

FIGURE 1. ASTM D1735 test results with Product A. The control panel is pictured on the far left.

FIGURE 2. ASTM D1735 test results with Product A. The control panel is pictured on the far left.

FIGURE 3. Image of the inside of the float coating test vessel. The vessel can accommodate several standard 4- by 12-in test panels (3- by 5-in test panels are pictured above).

FIGURE 4. Total view of the float coating test vessel. Test panel holder, funnel and tubing for bottom-up filling of the vessel, and drain spout can be seen.

tion capabilities where constant water fog is present. Treated 3- by 5-in SAE 1008 steel panels were tested for 500 h in the specified conditions before any corrosion was seen, as shown in Figure 1. In contrast, a control steel panel showed signs of corrosion within 24 h.

ASTM D1748

Product A was tested according to ASTM D1748 (with modifications noted above) to assess its corrosion protection in a constant condensing humidity environment. Treated steel panels were tested for over 1,950 h in the specified conditions before any corrosion was seen (Figure 2). In contrast, a control steel panel showed signs of corrosion within 24 h.

Laboratory Testing: Immersion Testing

Product A was tested in immersion conditions as noted above to assess the level of protection offered in a corrosive solution. As shown in Table 1, each panel that was treated with Product A witnessed a corrosion rate reduction of over 98%.

Laboratory Testing: Coating Thickness and Dosing Estimation

Immediately after application of Product A, a WFT gauge indicated a 175-µm (7-mil) film thickness on the surface of the test panel. After being allowed to drain for 1 h, the film was reevaluated to find a WFT of less than 25 µm (1 mil).

Through several trials, the necessary amount of product required to ensure a uniform coating thickness upon application was determined to be 5.5 L of Product A per m^2 of cross sectional tank area. In the case of tanks with a non-constant cross sectional area (e.g., frustum-shaped tanks), the average cross sectional area should be used. Through similar trials the required amount of product to properly coat vessel walls was determined to be 1 L per 20 m^2. The test apparatus is shown in Figures 3 and 4.

Real World Analysis

Select results from the elemental analysis testing of water used to apply Product A are provided in Table 2.

Conclusions

Traditional chemical treatment and epoxy coatings can be both expensive and time-consuming methods for protection and preservation of large vessels. In large volume systems, a float coat can offer a more economical corrosion protection

TABLE 1. IMMERSION TEST RESULTS

Sample	Treatment	Starting Mass (g)	Ending Mass (g)	Mass Loss (g)	Corrosion Rate (mpy)	Corrosion Reduction
1	Product A	23.8277	23.8234	0.0043	0.012	98.3%
2		23.8607	23.8567	0.0040	0.011	98.5%
3		23.8432	23.8381	0.0051	0.014	98.1%
4	Control	23.9134	23.6430	0.2704	0.73	N/A

solution than traditional chemical treatment by offering dosage rates based on surface area compared to costly dosage rates based on volume. Additionally, the minimally invasive application method can offer significant time savings when compared to traditional coating applications.

Humidity testing according to ASTM D1735 and D1748, and immersion testing based on ASTM G-31 showed excellent corrosion protection from the thin film left by Product A. Field application of the float coat product demonstrates the efficacy of these points. As shown in Table 2, this treatment does not impact the chemistry of the hydrotest water, allowing for water disposal to be carried out with only minimal disruption to normal disposal procedures and providing time and cost savings by significantly reducing or eliminating the expensive and lengthy process of handling large volumes of industrial waste.

The use of a float coat is an affordable and effective method for corrosion protection of large-volume vessels. Cost savings, time savings, and environmental considerations provide the basis for this novel treatment to vie with traditional preservation methods.

TABLE 2. SELECT RESULTS FROM HAZARDOUS CHEMICAL TESTING[9]

Chemical	Practical Quantification Limit (PQL)	Units	Result
Arsenic	0.09	mg/L	N/D(A)
Cadmium	0.15	mg/L	N/D
Chromium	0.1	mg/L	N/D
Lead	0.08	mg/L	N/D
Zinc	0.51	mg/L	N/D
Mercury	0.0005	mg/L	N/D
1,1-dichloroethene	6	µg/L	N/D
Chloroform	5	µg/L	N/D
Benzene	4	µg/L	N/D
Toluene	5	µg/L	N/D
Chlorobenzene	6	µg/L	N/D
Styrene	5	µg/L	N/D
Naphthalene	9	µg/L	N/D
4,4′-DDT	0.16	µg/L	N/D
Endrin	0.38	µg/L	N/D

References

1. G.H. Stilt, *Petroleum Engineering Handbook*, Chapter 13, "Oil Storage" (Richardson, TX: SPE International), pp. 505-523.
2. J.A. Veil, "Costs for Off-Site Disposal of Non-hazardous Oil Field Wastes: Salt Caverns Versus Other Disposal Methods," Argonne National Laboratory for U.S. Dept. of Energy, April 1997.
3. ASTM D1735, "Standard Practice for Testing Water Resistance of Coatings Using Water Fog Apparatus" (West Conshohocken, PA: ASTM International, 2014).
4. ASTM D1748, "Standard Test Method for Rust Protection by Metal Preservatives in Humidity Cabinet" (West Conshohocken, PA: ASTM, 2015).
5. ASTM G31-12A, "Standard Guide for Laboratory Immersion Corrosion Testing of Metals" (West Conshohocken, PA: ASTM, 2013).
6. APHA Method 3120B (1992), "Standard Methods for the Examination of Water and Wastewater" (Washington, DC: APHA, 1992).
7. EPA SW-846 Test Method 8260B, "Volatile Organic Compounds by Gas Chromatograpy/Mass Spectrometry (GC/MS)" (Washington DC: EPA, 1996).
8. EPA SW-846 Test Method 8081B, "Organochlorine Pesticides by Gas Chromatography" (Washington, DC: EPA, 2007).
9. "Water Analysis Report," Lonestar Technical Services LLC, CR46825S1, April 2016.

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JOHN WULTERKENS is a technical service engineer at Cortec Corp., St. Paul, Minnesota, USA, email: jwulterkens@cortecvci.com. He has two years of experience in the corrosion industry, working extensively on standard corrosion testing and advising on preservation and corrosion prevention applications.

CASEY HEURUNG is the technical service engineer at Cortec Corp., email: cheurung@cortecvci.com. He has 2½ years of experience in the corrosion industry. He holds a B.Sc. degree in chemistry. He performs routine testing, offers technical recommendations, and develops products for the company.

HOUSSAM SABRY is the manager of Corrosion & Inspection at ADGAS, Abu Dhabi, United Arab Emirates, email: houssam@adgas.com. He holds a B.Sc. degree in mechanical engineering and an M.Sc. degree in materials engineering. He has 23 years of experience in asset integrity, corrosion control, and inspection. Houssam has published more than 30 papers. He has been a NACE member since 2001 and a NACE Cathodic Protection Specialist since 2009.

Compatibility and Interactions Between Cathodic Protection and a Vapor Phase Corrosion Inhibitor

Calvin R. Pynn, *AEGIS Technical Systems LLC, Dubai, United Arab Emirates*
Khalil Abed, *Cortec Middle East, Dubai, United Arab Emirates*

The nature of the physical contact between the bottom plate of an above-ground storage tank and the underlying foundation/soil varies considerably over the area of a tank bottom and from tank to tank. This may vary from direct electrolytic contact between the plate and moist underlying soil to void spaces between the plate and the soil due to floor buckling and/or soil settlement. Cathodic protection (CP) is a proven corrosion mitigation technique where the target metal surface is in contact with a conductive electrolyte such as moist soil, but it will not be effective in void spaces where there is no electrolyte contact with the tank floor. Consequently, there is increasing application of vapor phase corrosion inhibitor (VCI) injection beneath tank bottoms to ensure corrosion is mitigated in the void spaces. The objective of this work was to evaluate the mutual compatibility and interactions between CP and a VCI where applied together in a liquid-phase environment. The work comprised laboratory experiments to quantitatively evaluate the effects of a particular amine carboxylate-based inhibitor and CP, when applied individually and jointly on an oxygen concentration corrosion macrocell in a salt water solution. The results indicate a beneficial synergistic effect between the particular inhibitor tested and CP, where the inhibitor enhances cathodic polarization to reduce CP current requirement, and CP reduction reaction appears to enhance the absorption and effectiveness of the inhibitor at the cathodic metal surface.

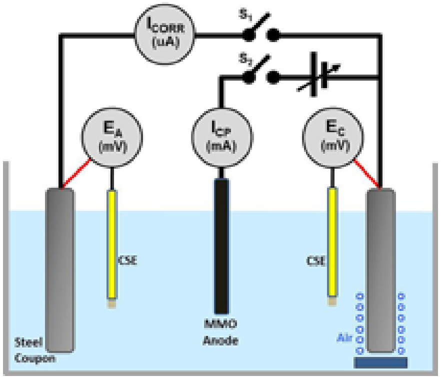


FIGURE 1 Test setup—schematic.

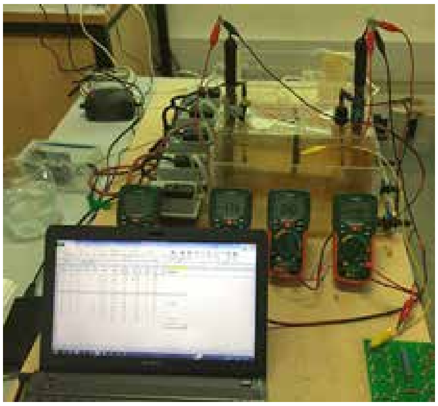


FIGURE 2 Test setup—physical arrangement.

The nature of the physical contact between the bottom plate of an above-ground storage tank and the underlying foundation/soil varies considerably over the area of a tank bottom and from tank to tank. This may vary from direct electrolytic contact between the plate and moist underlying soil to void spaces between the plate and the soil due to floor buckling and/or soil settlement.

Cathodic protection (CP) is an effective corrosion mitigation technique where there is an electrolytic contact between the tank bottom surface and the underlying soil (i.e., liquid-phase environment), but it cannot provide protection in the absence of an electrolyte, as is the case where there are gaps or voids between the tank bottom and soil, or where there is intermittent moisture in the soil contacting the tank bottom surface (i.e., vapor-phase environment).

Increasingly, vapor phase corrosion inhibitors (VCIs) are being injected beneath tank bottoms to mitigate the vapor-phase corrosion aspect. There are many types and chemistries of corrosion inhibitors that affect the electrochemical reactions at the metal-electrolyte interface. Each of these has specific properties that may or may not be compatible with CP or other corrosion prevention measures.

The objective of this work was to evaluate the mutual compatibility and interactions between CP protection and a particular VCI where applied together.

Test Setup and Procedure

The test method objective was to provide a quantitative evaluation of the effectiveness of CP and an amine carboxylate-based VCI when applied individually and jointly to mitigate the corrosion current in a liquid-phase corrosion "macro-cell."

An oxygen concentration cell between two carbon steel (CS) electrodes was deemed representative of the prevalent macro-cells that exist on tank bottoms. A salt water solution (3.6 L at 35 g sodium chloride [NaCl] per L) was used. A variable-output air pump forced air though a diffuser positioned below one of the CS electrodes to encourage a cathodic (reduction) reaction and create a potential difference with respect to the unaerated steel electrode. A mixed metal oxide Ti rod anode was positioned midway between the steel electrodes and powered by a variable direct current power supply. The schematic and physical arrangement of the test apparatus is depicted in Figures 1 and 2.

Preparatory Procedure

A preliminary preparatory procedure to reliably produce the macrocell consisted of the following steps:

1. The test container was cleaned and rinsed.
2. Salt water solution (3.6 L with 35 g NaCl per L) was prepared and placed in the test container.
3. Test rod metal surfaces were cleaned and sanded to NACE No. 1/SSPC-SP 5/Sa 3[1] finish.
4. Test rods were placed in solution, without bond, and allowed to soak for at least 16 h for each to reach a stable open-circuit potential (OCP).
5. Copper/copper sulfate ($Cu/CuSO_4$) reference electrodes (CSEs) were freshly prepared, tested to verify a <1 mV difference between them, and placed in the test apparatus.
6. The OCP of each test rod was measured and monitored to ensure their stability.
7. The test rods were bonded, and the bond current and potentials were monitored until they stabilized.
8. Aeration was started to cause a potential difference between the test rods, and adjusted until a steady state potential difference of 35 to 40 mV was achieved along with an associated corrosion current (i.e., I_{CORR}) of 350 to 400 μA.

Test 1—Effect of VCI on Active CP System

Following the preparatory procedure, this test consisted of the following steps:

1. The CP arrangement was energized, and the CP current (I_{CP}) was adjusted to mitigate I_{CORR} (i.e., reduce I_{CORR} to zero). As cathodic polarization increased, I_{CP} was further adjusted to maintain I_{CORR} at zero until a steady state was reached.
2. The first 3 g of inhibitor was added to the solution. The effect on the I_{CORR} was monitored, and I_{CP} was adjusted to maintain I_{CORR} at zero until a steady state was reached.
3. The inhibitor concentration was increased by adding another 3 g, the effect on I_{CORR} was monitored, and I_{CP} was adjusted to maintain I_{CORR} at zero until a steady state was reached.
4. The inhibitor concentration was increased by adding another 3 g, the effect on I_{CORR} was monitored, and I_{CP} was adjusted to maintain I_{CORR} at zero until a steady state was reached.
5. CP was de-energized and I_{CORR} was monitored until a steady state was reached.
6. The aeration was turned off and I_{CORR} was monitored until a steady state was reached.

Test 2—Effect of VCI Prior to Application of CP System

Following the preparatory procedure, this test consisted of the following steps:

1. The first 3 g of inhibitor was added to the solution. The effect on the I_{CORR} was monitored until a steady state was reached.
2. The inhibitor concentration was increased by adding another 3 g and the effect on I_{CORR} was monitored until a steady state was reached.
3. The inhibitor concentration was increased by adding another 3 g and the effect on I_{CORR} was monitored until a steady state was reached.
4. The CP arrangement was energized, and the I_{CP} was adjusted to mitigate I_{CORR} (i.e. reduce I_{CORR} to zero). As cathodic polarization increased, I_{CP} was adjusted further to maintain I_{CORR} at zero until a steady state was reached.
5. CP was de-energized and I_{CORR} was monitored until a steady state was reached.
6. The aeration was turned off and I_{CORR} was monitored until a steady state was reached.

Test Results

The results for Test 1 are illustrated in Figure 3. The results for Test 2 are illustrated in Figure 4.

Discussion of Results

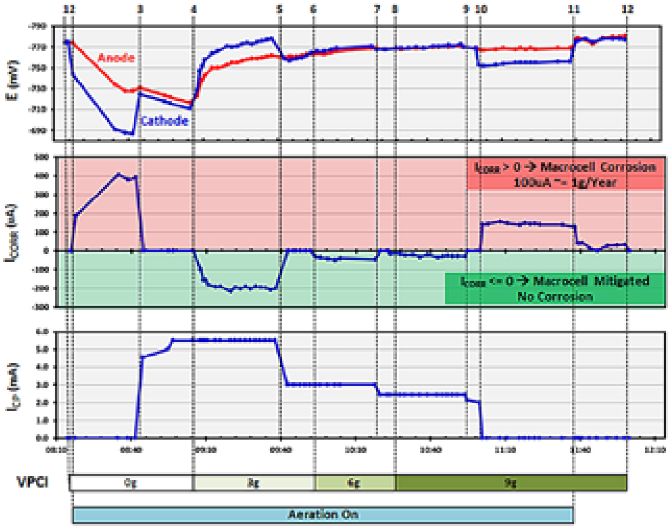
The Test 1 results are shown in Table 1. The Test 2 results are shown in Table 2.

Conclusions

The results indicate a beneficial synergistic effect between the VCI(x) tested and CP, where the inhibitor enhances cathodic polarization to reduce CP current requirement, and the CP reduction reaction appears to enhance the absorption and effectiveness of the inhibitor at the cathodic metal surface.

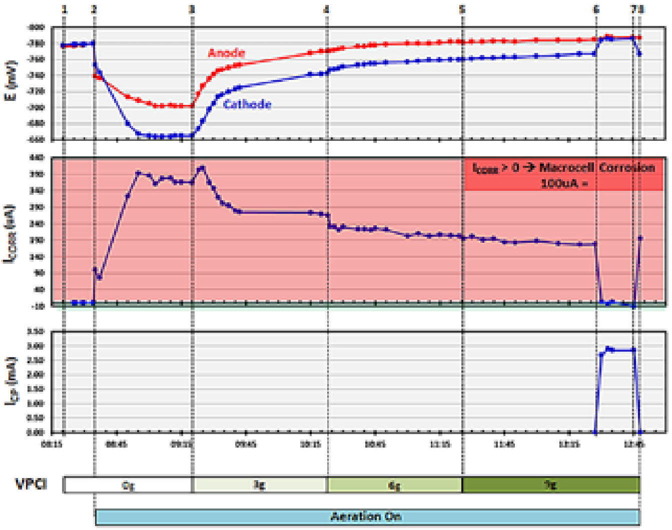
The following is a point-form summary of the conclusions drawn from this testing.

1. With respect to the VCI(x) tested:
   a. The VCI(x) tested is a "cathodic polarizer."
   b. As a cathodic polarizer, the VCI(x) tested reduced CP current requirement, and could thereby also enhance CP current distribution. Specifically, the CP current requirement of 5.5 mA to mitigate the corrosion cell before the addition of inhibitor was reduced by 45% with the first 3 g addition, 55% with further 3 g addition, and 60% with the final 3 g addition.
   c. At the concentrations tested, the VCI(x) substantially reduces, but does not completely mitigate the corrosion rate (i.e., I_{CORR}) in a liquid-phase macro-cell. Specifically, the original corrosion



Test Procedure Events
1. Test start—steady state coupon potentials following preparatory procedure
2. Aeration started to create stable macrocell with potential difference of -40 mV
3. CP output current energized and adjusted to reduce I_{CORR} to 0 µA
4. 3 g VCI(x) added to solution
5. CP output reduced to maintain I_{CORR} at 0 µA
6. 3 g VCI(x) added to solution
7. CP output reduced to maintain I_{CORR} at 0 µA
8. 3 g VCI(x) added to solution
9. CP output reduced to maintain I_{CORR} at 0 µA
10. CP de-energized
11. Aeration stopped
12. Test end

FIGURE 3 Test 1 results—effect of VCI on active CP system.



Test Procedure Events
1. Test start—steady state coupon potentials following preparatory procedure
2. Aeration started to create stable macrocell with potential difference of -40 mV between coupons and I_{CORR} of –375 µA
3. 3 g VCI(x) added to solution
4. 3 g VCI(x) added to solution
5. 3 g VCI(x) added to solution
6. CP output current energized and adjusted to reduce I_{CORR} to 0 µA
7. CP de-energized
8. Test end

FIGURE 4 Test 2 results—effect of VCI in the absence of CP.

rate of 375 µA was reduced by 27% with the first 3 g addition, 45% with further 3 g addition, and 52% with the final 3 g addition.

2. With respect to CP:
   a. CP can completely mitigate liquid-phase macrocell corrosion.
   b. CP appears to enhance the absorption and effectiveness of the inhibitor at the cathodic metal surface.

Caveats to Conclusions—Limitations of Testing

1. The test results revealed in this work apply to the specific VCI type and concentrations tested and are definitely not indicative of all inhibitors. For example, completely different results would be expected for "anodic inhibitor" chemistries.
2. There are many types and chemistries of corrosion inhibitors with varying application concentrations on the market having specific properties that differ from the VCI tested in this work. Each of these should undergo similar testing as that performed in this work to specifically evaluate their effectiveness and compatibility.
3. It must be emphasized that this work evaluates the effectiveness and compatibility in the liquid-phase exposure. It does not in any way reflect the effectiveness of the inhibitor to reduce corrosion in the vapor-phase for which it is primarily intended.
4. As inhibitors generally affect the electrochemical reactions at the metal-electrolyte interface, and therefore their potentials, the presence of any inhibitor in the electrolyte would be expected to affect the potential stability of permanent reference electrodes used for CP performance evaluation, and similarly, the potential of any galvanic anodes in the same environment.
5. It is recognized that the time between test stages was limited and therefore not sufficient for parameters to reach a true steady state before adjusting variables. These times should be extended in future work.

Acknowledgments

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Reference

1. NACE No. 1/SSPC-SP 5/Sa 3, "White Metal Blast Cleaning" (Houston, TX: NACE International).

Bibliography

Abed, K., P. Panchai, A. Gamdo. "Evaluation of Impressed Current Cathodic Protected API 650 Tank Bottoms in the Presence of Vapor Phase Corrosion Inhibitor." CORROSION 2016, paper no. 7600. Houston, TX: NACE International.

Al-Sulaiman, S., H. Sabri, R. Rahim. "Evaluation of Cathodic Protection System Criteria on Con-

TABLE 1. EFFECT OF VCI ON ACTIVE CP

Event	Observation
1	Both coupons were at –774 mV vs. CSE following the preparatory procedure.
2	A macrocell was created by the aeration to achieve a steady state potential difference of ~40 mV between coupons and an I_{CORR} of ~400 µA. The aeration caused potentials of both coupons to shift electropositive as a result of cathodic depolarization.
3	The application of CP with I_{CP} = 5.5 mA caused the cathode coupon to cathodically polarize toward the potential of the anode coupon, thereby reducing I_{CORR} to 0 µA to effectively mitigate the macrocell.
4	An initial 3 g of VCI(x) was added to the solution while I_{CP} was maintained at 5.5 mA. Both coupons shifted electronegative, indicating they were being cathodically polarized. The cathodic polarization of the cathode coupon exceeded that of the anode coupon, resulting in a "-ve" I_{CORR} value (i.e., ~ –200 µA).
5	I_{CP} was reduced to 3 mA to bring I_{CORR} to 0 µA.
6	Further 3 g of VCI(x) was added to the solution while I_{CP} was maintained at 3.0 mA. As was the case following Event 4, both coupons shifted electronegative, but not to the same magnitude as observed with the initial VCI(x) addition, resulting in a "-ve" I_{CORR} value (i.e., ~ –40 µA).
7	I_{CP} was reduced to 2.45 mA to bring I_{CORR} to 0 µA.
8	Further 3 g of VCI(x) was added to the solution while I_{CP} was maintained at 2.45 mA. As was the case following Event 6, both coupons shifted electronegative, but not to the same magnitude as observed with the initial VCI(x) addition, resulting in a "-ve" I_{CORR} value (i.e., ~–20 µA).
9	At Event 7, I_{CP} was reduced to 2.15 mA to bring I_{CORR} to 0 µA.
10	The CP system was de-energized and the cathode potential shifted electropositive and I_{CORR} increased to ~140 µA.
11	When the aeration was stopped, thereby eliminating the driving source for the macrocell, the potential of the cathode coupon approached that of the anode coupon (i.e., –774 mV vs. CSE), and I_{CORR} decreased to ~30 µA.

TABLE 2. EFFECT OF VCI IN THE ABSENCE OF CP

Event	Observation
1	Both coupons were at –777 V vs. CSE following the preparatory procedure.
2	A macrocell was created by the aeration to achieve a steady state potential difference of ~40 mV between coupons and an I_{CORR} of ~375 µA. The aeration caused potentials of both coupons to shift electropositive as a result of cathodic depolarization.
3	An initial 3 g of VCI(x) was added to the solution. Both coupons shifted electronegative, indicating they were being cathodically polarized, and I_{CORR} decreased to ~275 µA.
4	Further 3 g of VCI(x) was added to the solution. Both coupons shifted electronegative, indicating they were being cathodically polarized, and I_{CORR} decreased to ~205 µA.
5	Further 3 g of VCI(x) was added to the solution. Both coupons shifted electronegative, indicating they were being cathodically polarized, and I_{CORR} decreased to ~180 A.
6	The application of CP with I_{CP} = 2.85 mA caused the cathode coupon to cathodically polarize toward the potential of the anode coupon, thereby reducing I_{CORR} to 0 µA to effectively mitigate the macrocell.
7	The CP system was de-energized, the cathode potential shifted electropositive, and I_{CORR} increased back to ~200 µA.

structed Tanks Over Bituminous Sand Mix Layer. 14th Middle East Corrosion Conference, paper no. 63-CP-10. Manama, Bahrain: NACE, 2012.

Barnawi, I.Y. "Comparison of Corrosion Attack on Tank Bottoms with and without Cathodic Protection." *MP* 51, 8 (2012): pp. 31-35.

Chatterjee, B. "Prevention of External (Soil Side) Corrosion on Storage tank Bottom Plates by Cathodic Protection System." CORROSION 2008, paper no. 8058. Houston TX: NACE, 2008.

"Corrosion Rate of a Double-Tank Interstitial Space." *Pipeline & Gas J.* 32, 6 (2005): pp. 49-50.

Gandhi, A. "Storage Tank Bottom Protection Using Vapor-phase Corrosion Inhibitors." *MP* 40, 1 (2001): pp. 28-30.

Meroufel, A., M. Al-Hajri, K. Abed. "Mitigation of Soil-Side Corrosion on Storage Tank Bottoms in the Absence or Deficient of CP System."16th Middle East Corrosion Conference, paper no. MECCFEB16-7995. Manama, Bahrain: NACE, 2016.

Miksic, B.A., A.Y. Furman, M. Kharshan. "Storage Tank Protection Using Volatile Corrosion Inhibitors." *MP* 45, 6 (2006): pp. 34-37.

Rials, S.R., J.H. Kiefer. "Evaluation of Corrosion Prevention Methods for Aboveground Storage Tank Bottoms." *MP* 32, 1 (1993): pp. 20-25.

Yu, Xiaming (Andy). "Evaluation of the Tank Bottom Corrosion and CP Effectiveness at a Saudi Aramco Crude Oil Tank Farm." 13th Middle East Corrosion Conference, paper no. 10043. Bahrain, Manama: NACE, 2013.

Whited, T. "Corrosion Slowed On Tank Bottoms: Vapor Corrosion Inhibitors Used To Mitigate Corrosion Rate of a Double-Tank Interstitial Space." *Pipeline & Gas J.* 32, 6 (2005).

Whited, T. "Mitigation of Soil Side Corrosion on Double Contained Aboveground Storage Tank Floors." Cortec Corp. Supplement to *MP* (2011): pp. 7-10.

Whited, T., X. Yu, R. Tems. "Mitigating Soil-Side Corrosion on Crude Oil Tank Bottoms Using Volatile Corrosion Inhibitors." CORROSION 2013, paper no. 2242. Houston TX: NACE, 2013.

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CALVIN R. PYNN is the founder and senior specialist at Aegis Technical Systems, LLC, Dubai, United Arab Emirates, email: calvin.pynn@eim.ae. He is a graduate of the Ryerson Polytechnical Institute, Toronto, Ontario, Canada Electrical Engineering Technology Program and has been a member of NACE International since 1978. He is a NACE-certified Senior Corrosion Technologist and Cathodic Protection Specialist and is an instructor in the NACE Cathodic Protection Program. He specializes in the application of electrochemical corrosion control systems and has worked extensively in the oil and gas, chemical process, water treatment, and civil engineering industries in Canada and the Middle East. He has been based in Dubai since 1992, primarily focusing on extending the durability of reinforced concrete, industrial and marine structures in the Arabian Gulf region.

KHALIL ABED is the regional manager of Cortec Middle East, Dubai, United Arab Emirates, email: kabed@cortecme.com. Prior to his current position, he held several technical and managerial positions at multinational companies in the construction and oil and gas sectors. He has an M.Sc. degree in mechanical engineering from the American University of Sharjah. He is a member of NACE International. *MP*

High-Performance Water-Based Coating Enhanced with Nano-Vapor Corrosion Inhibitors

Markus Bieber, *Cortec Corp., St. Paul, Minnesota, USA*

The use of single-component water-based coatings for protection of military metal substrates continues to grow due to their low odor, health and safety advantages, easy cleanup, and environmental friendliness. Nevertheless, the challenge remains to find alternatives to the traditional chromate, zinc, or similar heavy metal-type corrosion inhibitors that tend to rely on passivation or sacrificial cathodic protection. Additionally, ongoing regulatory developments, which require lower volatile organic compounds and elimination of carcinogenic materials, continue to tighten the use of products containing these heavy metals, thus forcing the need for alternative technologies. The use of nano-vapor phase corrosion inhibitors provides an attractive alternative by adsorbing onto the metal substrate and filling the voids or micro-crevices of the substrate and preventing corrosion from starting or growing once the surface of the coating has been damaged. This technology has been proven effective in single-component water-based coatings at a dry film thickness of 1 mil (25 μm).

In a 2002 study by NACE International,[1] the cost of corrosion for the U.S. Department of Defense (DoD) was estimated to be in excess of $20 billion. Traditional corrosion control methods for protecting metal substrates in the military include chromate, zinc, and other heavy metals in inhibitors working in conjunction with passivation or cathodic protection.[2] An environmentally friendly, effective alternative involves the use of nano-vapor phase corrosion inhibitors (VCIs) in coatings used to protect these assets.[3-4]

VCIs and Coatings

How VCIs Work in a Coating

VCIs are formulated into a coating through a complex development process that involves determining chemical compatibility of the VCIs with the other components of the coating, such as the resin, solvents, pigments, and other additives used for a variety of reasons. VCIs work by adsorbing onto the metal surface in a nonreactive attractive capacity; in other words, they are attracted to the metal through the particle charge.[5]

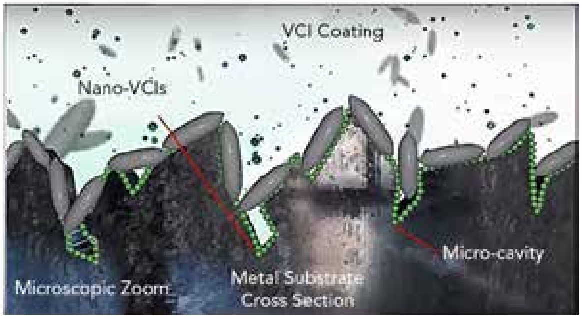

FIGURE 1 Use of traditional inhibitors with larger platelets can leave gaps in which corrosion can occur.

How VCIs Compare to Traditional Inhibitors

VCIs compare with traditional inhibitor systems by using smaller particles as well as relying not only on contact inhibition but also vapor phase inhibition, providing more complete coverage and protection of the surface. This is illustrated in Figure 1.

The larger platelets are representative of traditional inhibitors that are unable to fill the micro-crevices, leaving gaps where corrosion can start and/or grow.[6]

Types of Coating Systems that Use VCIs

VCIs can be used with most coating systems. There are many variations of VCIs and the key is to choose the correct VCI for the corresponding coating system by checking compatibility, effectiveness, and processability.

Environmental Advantages of VCIs over Traditional Inhibitors

Traditional inhibitors containing heavy metals are becoming increasingly more regulated and often are no longer allowed to be used due to the negative impact they have on the environment and as carcinogens for workers exposed to them. The environmental advantages of using VCIs are that they are nontoxic, do not contain heavy metals, and have no adverse effect due to their low usage concentrations. VCIs have long been used in other products such as polyethylene films, foams, powders, and liquids to provide a vapor phase of corrosion protection without impacting the environment.

Experimental Procedures

This study examines the effectiveness of various types of corrosion inhibitors in a waterborne styrenated acrylic coating, based on salt fog results (ASTM B117[7]). All of the samples were made using high-speed dispersion.

Each coating was applied in triplicate on 4 by 12-in cold-rolled steel (CRS) panels (SAE 1010), using a 40 RDS† draw down bar. This produced a dry film thickness (DFT) of 1.0 mils +/– 0.2 mils. Tables 1 and 2 show the list of prepared samples.

Testing Procedures

Panels were prepared according to ASTM B117 and allowed to cure at ambient temperature for seven days. After the curing cycle, the panels were scribed with a single diagonal scribe per ASTM D1654.[8] All of the edges and backs of the panels were taped to prevent any corrosion creep from uncoated surfaces. Panels were then placed in a 5% sodium chloride (NaCl) salt fog chamber, per ASTM B117. The test panels were checked periodically for blisters, creep from scribe, and degree of rusting.

Results

The purpose of this experiment was to investigate the effectiveness of nano-VCIs when added to waterborne acrylics. The ultimate goal was to achieve 1,000 h in a salt fog chamber (ASTM B117), on CRS, with a high gloss clearcoat of less than 2.0 mils DFT. Normally this kind of performance can only be achieved with highly pigmented coatings using corrosion inhibitors that are toxic, or at the very least not environmentally friendly.

The control panels failed at approximately 168 h in the salt fog cabinet, as can be seen in Figure 2 and Table 3.

Figure 3 and Table 4 show the results of the 700-h salt fog test; Figure 4 and Table 5 show the results at 1,000 h.

TABLE 1. LIST OF COATING FORMULATIONS

Sample No.	Description	Corrosion Inhibitor	Percent of total formula weight (%)	Coating thickness (mils)
1	Control	D	0	0.9-1.2
2	Exp. 1	A	3	0.9-1.2
3	Exp. 3	A+C	5	0.9-1.2
4	Exp. 2	B	3	0.9-1.2
5	Exp. 4	B+C	3	0.9-1.2

TABLE 2. CORROSION INHIBITOR DETAIL

Corrosion Inhibitor	Description
D	Organic/inorganic corrosion inhibitor
A	Amino carboxylate salt
A+C	Amino carboxylate salt + nano-inhibitor
B	Liquid sol gel
B+C	Liquid sol gel + nano-inhibitor

TABLE 3. ASTM B117, 168 H SALT FOG RESISTANCE

Sample No.	Film Thickness (mils)	Corrosion Rating(A)	Scribe Rust(B)
1	0.9-1.2	5	5
2	0.9-1.2	8	5
3	0.9-1.2	9	9
4	0.9-1.2	8	8
5	0.9-1.2	10	10

(A)ASTM D1654, Procedure B rating of unscribed areas: 10 = no corrosion, 5 = 11 to 20% corrosion, 0 = 75%+ corrosion.

(B)ASTM D1654, Procedure A rating of failure at scribe: 10 = no creepage, 5 = 0.125-0.1875 in., 0 = 0.625+ in.

Coatings

With the DoD estimating that corrosion costs in the military are in excess of $20 billion, there is a need for environmentally friendly, low volatile organic compounds, waterborne coatings that can be applied at a thin film thickness (1.0 mils)

FIGURE 2 Control panels failed after 168 h in the salt fog cabinet.

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†Trade name.

TABLE 4. ASTM B117, 700 H SALT FOG RESISTANCE

Sample No.	Film Thickness (mils)	Corrosion Rating(A)	Scribe Rust(B)
1	0.9-1.2	5	5
2	0.9-1.2	8	5
3	0.9-1.2	9	9
4	0.9-1.2	8	8
5	0.9-1.2	10	10

(A)ASTM D1654, Procedure B rating of unscribed areas: 10 = no corrosion, 5 = 11to 20% corrosion, 0 = 75%+ corrosion.
(B)ASTM D1654, Procedure A rating of failure at scribe: 10 = no creepage, 5 = 0.125-0.1875 in., 0 = 0.625+ in.

TABLE 5. ASTM B117, 1,000 H SALT FOG RESISTANCE

Sample No.	Film Thickness (mils)	Corrosion Rating(A)	Scribe Rust(B)
1	0.9-1.2	0	0
2	0.9-1.2	5	2
3	0.9-1.2	3	4
4	0.9-1.2	3	4
5	0.9-1.2	9	9

(A)ASTM D1654, Procedure B rating of unscribed areas: 10 = no corrosion, 5 = 11to 20% corrosion, 0 = 75%+ corrosion.
(B)ASTM D1654, Procedure A rating of failure at scribe: 10 = no creepage, 5 = 0.125-0.1875 in., 0 = 0.625+ in.

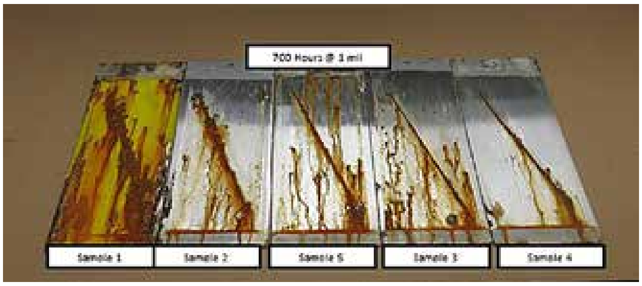

FIGURE 3 Control panels after 700 h in the salt fog cabinet.

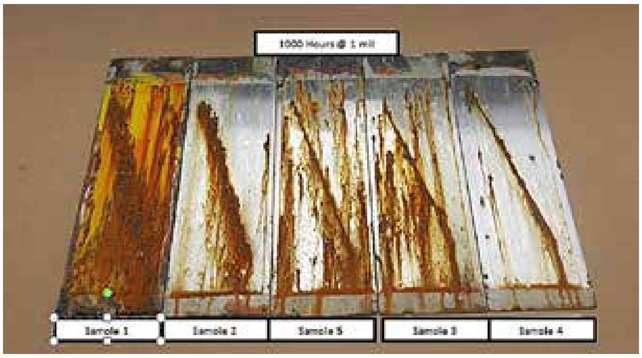

FIGURE 4 Control panels after 1,000 h in the salt fog cabinet.

and provide excellent corrosion protection.

This article shows, through research, that the combination of nano-VCIs and nontoxic metal complex inhibitors form a synergistic effect that now allows for water-based acrylics to reach 1,000 h of salt fog testing at less than 1.5 mils (ASTM B117). The direct to metal aspects of these coatings results in direct cost savings by reducing the amount of material needed, reducing the application time and labor due to fewer coats, and finally, reducing the time and expense of equipment cleanup due to the environmentally friendly nature of the waterborne systems. Applications range widely from equipment to vehicles to infrastructure where chemical agent-resistant coatings are not specified or required.

References

1. "Corrosion Costs and Preventive Strategies in the United States," G.H. Koch, et al., FHWA Report no. RD-01-156 (Houston, TX: NACE International, 2002).
2. N.P. Andreeva, et al., "To the Adsorption of Volatile Corrosion Inhibitor N,N-Diethylaminopropionitrile on Iron," *Zashchita Metallov* 32, 4 (1996): pp. 437-440.
3. Y.I. Kuznetsov, et al., "Inhibiting Action and Absorption of Beta-Aminoketones on Metals," *Zashchita Metallov* 32, 5 (1996): pp. 528-533.
4. K.Y. Blohowiak, et al., "Hybrid Nanostructured Sol-Gel Coating Systems," Proc. Smart Coatings Symposium, Orlando, FL (2007).
5. B.A. Miksic, "Use of Vapor Phase Inhibitors for Corrosion Protection of Metal Products," CORRSION/83 paper no. 308 (Houston, TX: NACE, 1983).
6. N.N. Andreev, T.V. Fedotova, "Volatile Corrosion Inhibitors Based on Ethanolamines," *Zashchita Metallov* 33, 5 (1997): pp. 521-527.
7. ASTM B117, "Standard Practice for Operating Salt Spray (Fog) Apparatus" (West Conshohocken, PA: ASTM International, 2016).
8. ASTM D1654, "Standard Test Method for Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments" (West Conshohocken, PA: ASTM, 2016).

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MARKUS BIEBER is the director of sales—High Performance Coatings & Additives at Cortec Corp., St. Paul, Minnesota, USA, email: mbieber@cortecvci.com. He has spent more than 20 years in product and sales management in the coatings industry, with a focus on providing customers with value-added coating solutions. He is a member of NACE International.