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SUPPLEMENT TO **JUNE 2019**

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CORROSION PREVENTION AND CONTROL WORLDWIDE

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CORROSION PROTECTION IN AN OIL SYSTEM WITH WATER INGRESS

Application of Inhibitors for Contaminated Environments

Use of Volatile Corrosion Inhibitors in Coatings

Protecting Equipment from Corrosion with Enhanced Packaging

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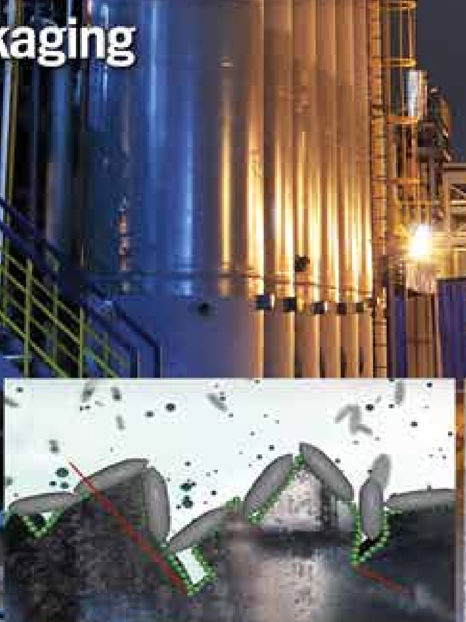

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VOLATILE CORROSION INHIBITORS

Economic, Environmentally Friendly Solutions for Corrosion Prevention and Control

Vapor phase and volatile 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. 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.

The Use of VCIs in Conjunction with or Replacement of Traditional Corrosion Inhibitors

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

The use of traditional corrosion inhibitors in paints and coatings continues to be challenged from both an environmental and performance aspect. End users are demanding better corrosion performance and in many formulations this cannot be achieved with traditional zinc or chromate-type inhibitors. The use of vapor corrosion inhibitors in coating formulations has shown that in many systems, they can replace the older technology or significantly improve the performance of the system by working in synergy with the existing inhibitors.

Vapor phase corrosion inhibitors (VCIs) are a corrosion inhibitor technology that is comprised of very small particles that are attracted to a metal substrate. Once the particles attach to the metal substrate through adsorption, they prevent a corrosion cell from forming. They come in various formulations that are dependent on the type of system they will be used in; for example, films, oils, coatings, cleaners, etc. There are also a variety of formulations that provide protection in ferrous, nonferrous, or multimetal applications. Other variables include the amount of vapor phase compared to contact phase inhibitors.[1] VCIs are widely used throughout a broad range of industries and applications ranging from automotive to processing to preservation and have saved billions of dollars of corrosion-expenses.

VCIs as Alternative Corrosion Inhibitor Technologies

The use of VCIs as alternative corrosion inhibitor technologies in coatings is not a new concept. In the last few years, however, with the growing environmental pressures to reduce the use of traditional inhibitors containing heavy metals, they have gained in popularity.[2]

VCIs as a category are very broad and can be made up of thousands of combinations of raw materials that can have varying rates of effectiveness. Commonly used terms, such as amine carboxylates, cover a broad range of potential formulations. Depending on the formulation, they can vary in their functionality as far as contact vs. vapor phase inhibition. When choosing the right VCI package to formulate into a coating, it is critical to find not only the package that is compatible with the coatings carrier (solvent or water) but also the resin system.

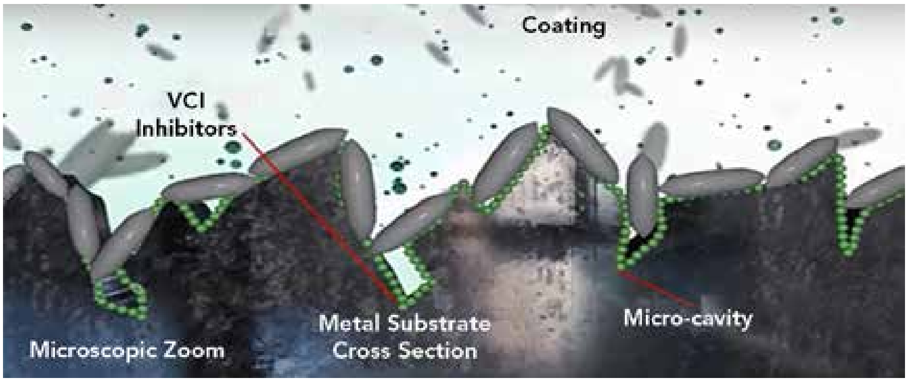

FIGURE 1 Microscopic surface view.

Choosing the wrong inhibitor package can lead to a variety of issues in the coating itself, which include gelling, phase separation, and flocculation. Once these issues have been eliminated, the next stage is testing to determine at which level there is an improvement in the corrosion performance, which is typically done using the salt fog test standard (ASTM B117[3]).

Since VCI particles have a polar attraction to the metal substrate, this allows them to work in the coating without negatively impacting other components of the coating such as defoamers, wetting agents, leveling agents, etc. VCIs are typically added to the formulation in very small amounts by weight of the overall formula. The typical range is from 0.5% to 3%.

The particle size of the VCIs is very small in comparison to the traditionally used inhibitors (Figure 1). This allows the VCIs to migrate into the smaller voids more effectively.

Once the VCIs have adsorbed onto the surface of the metal, they provide an effective barrier that is hydrophobic and prevents moisture from getting through to the metal surface.

Consequently, this prevents the formation of a corrosion cell and renders the moisture ineffective.[4]

Experimental Procedure

These studies examine the effectiveness of various types of corrosion inhibitors in single-component, waterborne acrylic coatings, based on salt fog results (ASTM B117).

TABLE 1 Inhibitor Combinations in the Study

Additive	ID		Panel	#		Panel	#		Panel	#		Panel	#		Panel	#
Inhibitor Co 1	A	Inhibitor Co 1(3%) + VCI Inhibitor (3%)	A+A2	1	Inhibitor Co 2(3%) + VCI Inhibitor (3%)	A1+A2	1	Inhibitor Co 1 @ 5%	A	1	Inhibitor Co 2 @ 5%	A1	1	VCI Inhibitor	386	1
Inhibitor Co 1	B			2			2			2			2			2
Inhibitor Co 1	C			3			3			3			3			3
Inhibitor Co 1	D		A+B2	1		A1+B2	1		B	1		B1	1		ECO386	1
				2			2			2			2			2
Inhibitor Co 2	A1			3			3			3			3			3
Inhibitor Co 2	B1		A+C2	1		A1+C2	1		C	1		C1	1			
Inhibitor Co 2	C1			2			2			2			2			
Inhibitor Co 2	D1			3			3			3			3			
			A+D2	1		A1+D2	1		D	1		D1	1			
Inhibitor Co 1	A2			2			2			2			2			
Inhibitor Co 2	B2			3			3			3			3			
Inhibitor Co 3	C2		B+A2	1		B1+A2	1									
Inhibitor Co 4	D2			2			2									
				3			3									
			B+B2	1		B1+B2	1									
DFT1.0-1.2 on all panels				2			2									
				3			3									
			B+C2	1		B1+C2	1									
				2			2									
				3			3									
			B+D2	1		B1+D2	1									
				2			2									
				3			3									
			C+A2	1		C1+A2	1									
				2			2									
				3			3									
			C+B2	1		C1+B2	1									
				2			2									
				3			3									
			C+C2	1		C1+C2	1									
				2			2									
				3			3									
			C+D2	1		C1+D2	1									
				2			2									
				3			3									
			D+A2	1		D1+A2	1									
				2			2									
				3			3									
			D+B2	1		D1+B2	1									
				2			2									
				3			3									
			D+C2	1		D1+C2	1									
				2			2									
				3			3									
			D+D2	1		D1+D2	1									
				2			2									
				3			3									

ASTM B117 tests products in a 5% sodium chloride (NaCl) salt fog chamber with continuous exposure as per the ASTM standard.

Each coating was applied on cold-rolled steel (CRS) panels (SAE 1010), using a 0.40 drawdown bar. Dry film thicknesses (DFTs) yielded were 0.9 to 1.2 mils (23 to 30 µm). Each coating/inhibitor combination was applied in triplicate. Coated panels were air dried in lab conditions at an ambient temperature of 70 °F (20 °C) and 50% relative humidity for seven days before being placed into the B117 chamber.

A matrix (Table 1) was designed to track the various coating/inhibitor combinations as follows:

- Additive variables:
    - Eight different types of "traditional" inhibitors containing zinc phosphates, calcium phosphates, strontium phosphates, etc.
        - Products are typically added at a wt% (5%) of the total coating formula.
    - Four different types of VCIs containing proprietary blends of amine carboxylates.
        - Products are typically added at a wt% (0.5 to 3%) of the total coating formula. For this experiment, they were added at 3%.
- Coatings contained:
    - 32 combinations of traditional inhibitors and VCIs.
        - Products were added at a reduced wt% (3%) of the total coating formula plus the VCIs at 3%.
    - Two combinations with VCIs
        - Products were added to a wt% of 0.5 to 2.0% (Figure 2).

Results

The results shown in Table 2 were based on a visual inspection and rating. From the testing that was done, it is clear that VCIs are a viable solution for use as corrosion inhibitors in coatings. Figure 2 shows that VCIs by themselves have the ability to provide excellent corrosion protection. As evidenced, salt spray performance in many cases was matched by reducing the percentage of traditional inhibitor used (recommended dosage of 5% by total formula weight to 3% by total

FIGURE 2 VCIs A and B only, 30 days = 720 h.

formula weight) and adding the VCI (at 3% by total formula weight). This is illustrated in Table 2 with the positive performing synergies highlighted. These synergies allow for reduced usage of inhibitors that may have to meet stricter environmental limits while possibly providing cost savings as well.

Combinations of B2 with various traditional inhibitors seemed to consistently provide comparable results, while the use of the VCI only provided the best results in this system.

Conclusions

Customers are becoming more and more demanding and are expecting their coatings to last longer. With the ongoing performance and environmental challenges in the coatings industry, there continues to be a need for new technologies that can provide better performance.

Stricter regulations limiting the use of certain products continues to make this more difficult as formulators are having to find alternatives to the products that have been used for many years. This article shows, through research, that the use of VCIs can match or improve the corrosion resistance of coatings either used by themselves or in combination with existing inhibitor technologies, thus reducing the environmental concerns without sacrificing performance.

Acknowledgments

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This article is based on CORROSION 2019 paper no. 13079, presented in Nashville, Tennessee, USA.

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TABLE 2 Combination Results

Hours	Combo	Hours	Standard	Result		Hours	Combo	Hours	Standard	Result
480	A+A2	480	A	worse		480	A1+A2	480	A1	worse
480	A+B2	480	A	worse		480	A1+B2	480	A1	same
480	A+C2	480	A	worse		480	A1+C2	480	A1	worse
480	A+D2	480	A	worse		480	A1+D2	480	A1	worse
480	B+A2	480	B	worse		480	B1+A2	480	B1	same
480	B+B2	480	B	same		480	B1+B2	480	B1	same
480	B+C2	480	B	worse		480	B1+C2	480	B1	same
480	B+D2	480	B	worse		480	B1+D2	480	B1	worse
480	C+A2	480	C	worse		480	C1+A2	480	C1	worse
480	C+B2	480	C	worse		480	C1+B2	480	C1	same
480	C+C2	480	C	worse		480	C1+C2	480	C1	worse
480	C+D2	480	C	worse		480	C1+D2	480	C1	worse
480	D+A2	480	D	worse		480	D1+A2	480	D1	worse
480	D+B2	480	D	same		480	D1+B2	480	D1	same
480	D+C2	480	D	worse		480	D1+C2	480	D1	worse
480	D+D2	480	D	worse		480	D1+D2	480	D1	worse
		720	VCI A	better						
		720	VCI B	better						

Notes: A, B, C, and D are traditional inhibitors; A1, B1, C1, and D1 are traditional inhibitors; VCI A and VCI B are VCIs. The positive performing synergies are highlighted.

Application of Vapor Phase Corrosion Inhibitors for Contaminated Environments

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Boris A. Miksic, FNACE,
Cortec Corp., St. Paul, Minnesota, USA

Availability and accessibility to clean water for industrial applications such as hydrostatic pressure testing of pipelines, vessels, and plumbing distribution systems have been a challenging task, especially when the job sites are in remote locations. These circumstances have forced the use of contaminated water containing, for example, large amounts of chloride. Hydrostatic testing of metallic equipment is an important method for quality control of parts, after production and during use. When contaminated water is used in these tests, corrosion of the metallic components of the system during and after testing become a major concern; therefore, application of an inhibiting system is required. Vapor-phase corrosion inhibitors (VCIs) can be added to water in small concentrations to prevent corrosion during testing, or wet storage and after testing. These inhibitors are to prevent corrosion of metallic components in three phases: within the solution, at the water line, and above the water line.

Three commercially available corrosion inhibitors were evaluated in this study to optimize the best combination of inhibitors to minimize the corrosion of these multi-metallic component systems. Laboratory studies presented in this article show the effectiveness of VCI products in both fresh and salt water applications. Results confirmed the effectiveness of VCI products in various water chemistries including fresh and salt water. The average corrosion rate dropped from ~10 mpy for salt solution to less than 1 to 1.6 mpy when various inhibitors were added. However, the effectiveness of these inhibitors is remarkable in the fresh water (less than 0.4 mpy). Exposure of the steel samples to these inhibitors did not show any loss in mechanical properties. Both strength and ductility of the low carbon steel samples were maintained. Adsorption energy for these inhibitors was about –21,520 to –24,970 J/mol, indicating a strong physisorption mechanism.

The application of an inhibitor in any water system requires compliance with the Clean Water Act and the National Pollutant Discharge Elimination System (NPDES). The three corrosion inhibitors investigated were water-based, bio-based, environmentally friendly, and can be effective replacements for toxic nitrite, chromate or hydrazine-based inhibitors and satisfy all the required environmental compliance regulations.

Hydrostatic pressure testing of metallic equipment such as pipes, vessels, and valves is an important method for quality control of parts, after production and during use in order to demonstrate the strength and integrity of the systems.[1] This test is a key part of ensuring that they are fit for purpose depending on factors such as contact time, chemicals used, oxygen, and bacteria. Water is the most common media to be used in this test; however, corrosion of the metal during and after testing is a concern because the water is typically left in pipelines from a couple of days to months. The challenge is that hydrostatic test water is corrosive, and disposal of the water is costly. Hydrostatic test water contains micro-organisms, oxygen, and sediment that are known to accelerate corrosion progression. Also, because of the large volume of water used, treatment can be very expensive. In some cases, equipment that has gone through a hydrostatic test will also be stored for future use or shipped long distances. This storage may take place while water is still inside the equipment (wet storage) or even after draining.[2-4] Therefore, a pipeline undergoing a hydrostatic test may become quite vulnerable to general corrosion, crevice and pitting corrosion, stress corrosion cracking, differential aeration corrosion, or microbially induced corrosion.[2] Corrosion caused by any one or a combination of these mechanisms may reduce pipeline service life and in extreme cases make it unfit for purpose.

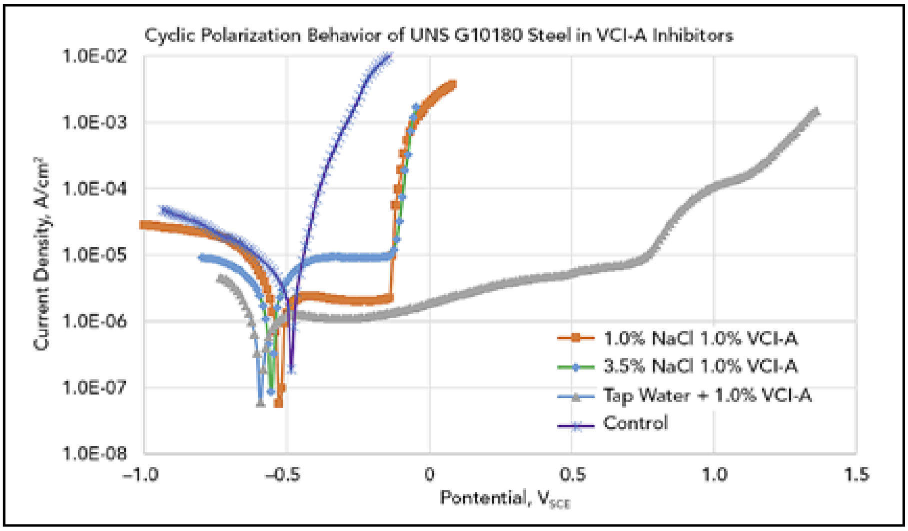

FIGURE 1 Cyclic polarization behavior of UNS G10180 steel in 1.0% VCI-A at different aqueous solutions.

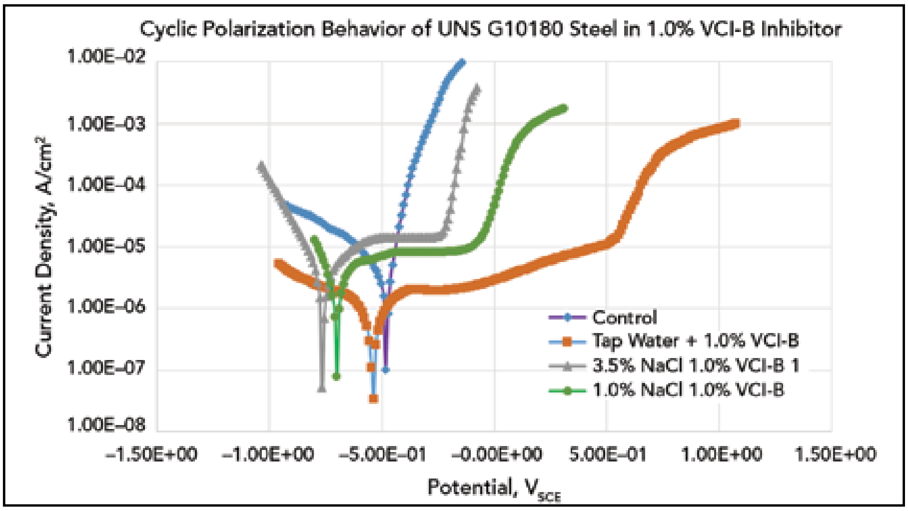

FIGURE 2 Cyclic Polarization behavior of UNS G10180 steel in 1.0% VCI-B at different aqueous solutions.

With the growing shortage of fresh water resources, it is often preferrable to utilize seawater as supplement water of recirculating cooling water systems.[2-3] But seawater is an electrolyte solution with multiple salts, mainly 3.0 to 5.0% sodium chloride (NaCl); a pH value of ~8; and dissolves a certain amount of oxygen.[1] Due to its chemistry, seawater easily corrodes pipelines. So the key to seawater utilization is to solve piping and equipment corrosion problems in the seawater environment by modifying its chemistry with the addition of corrosion inhibitors.

Corrosion and corrosion inhibition of steel have received enormous attention for recirculating cooling water systems.[5-7] The common methods to control and prevent metal equipment corrosion are using resistant material, using a cooling water anticorrosion coating, increasing the pH value of the cooling water operation, and adding corrosion inhibitor.[6-9] Among these methods, using resistant material can protect metal equipment effectively, but the expense is too high. The technology of an anticorrosion coating method is complex and applies to local anticorrosion in the system. Increasing water pH makes mild steel deactivate easily. Adding corrosion inhibitor can protect the system and it is economical and practical.[7] After the completion of a hydrostatic test, the water must be discharged, often with environmental considerations due to toxicity or excessive chemicals when inhibitors are added.[8]

The development of seawater corrosion inhibitor goes from inorganic to organic, from single to compound, from single inhibition type, to mixed inhibition type and other electrochemical method combination processes.[8] Many organic molecules exhibit high anticorrosion potential, but they pollute the environment during their synthesis and applications.[7-9] The effect of a single seawater corrosion inhibitor is unsatisfactory in general, so two or several types used in conjunction improve inhibition efficiency.

Therefore, to control corrosion and bacterial growth in the pipeline during hydrostatic pressure tests and future storage, the test water may be treated with corrosion inhibitors and other chemical compounds to manage and control corrosion activities. Commonly used chemicals are biocides that kill the micro-organisms and prevent the formation and growth of bacteria and other organisms in the seawater. Corrosion inhibitors are used to retard general corrosion when residual oxygen is available, and oxygen scavengers are used to reduce the amount of oxygen available for corrosion and bacterial growth. Different classes of corrosion inhibitors may be used to protect systems from corrosion, including inorganic or organic. Inorganic inhibitors include nitrites, phosphorous-based compounds, and others. Organic inhibitors are the products formulated from molecules constructed from of carbon, hydrogen, oxygen, and nitrogen atoms. Vapor-phase corrosion inhibitors (VCIs) described in this article are organic-based blends. The mechanism of the corrosion protection of organic inhibitors includes the formation of a thin, sometimes monomolecular layer on the metal, which is a protective barrier to aggressive ions.[4-5] In the majority of cases, organic components form a physical bond with the metal substrate. Formulations can include components with other functionalities for added protective capabilities. The main difference of the VCI products vs. non-VCI products is the presence in the formulation of an ingredient with moderately high vapor pressure that can prevent corrosion in the vapor space without applying the VCI directly to the metal surface.[9-10] The typical examples of this class are organic amines and their salts with carboxylic acids (amino-carboxylates). The advantage of VCIs are that the volatilized molecules can penetrate hard to-reach spaces. When they reach the metal, the VCI attaches to it by the active group, creating a strong physisorption mechanism. After the completion of a hydrostatic test, the water must be discharged and be in compliance with environmental restrictions. It is required to comply with the Clean Water Act and the National Pollutant Discharge Elimination System (NPDES).[8]

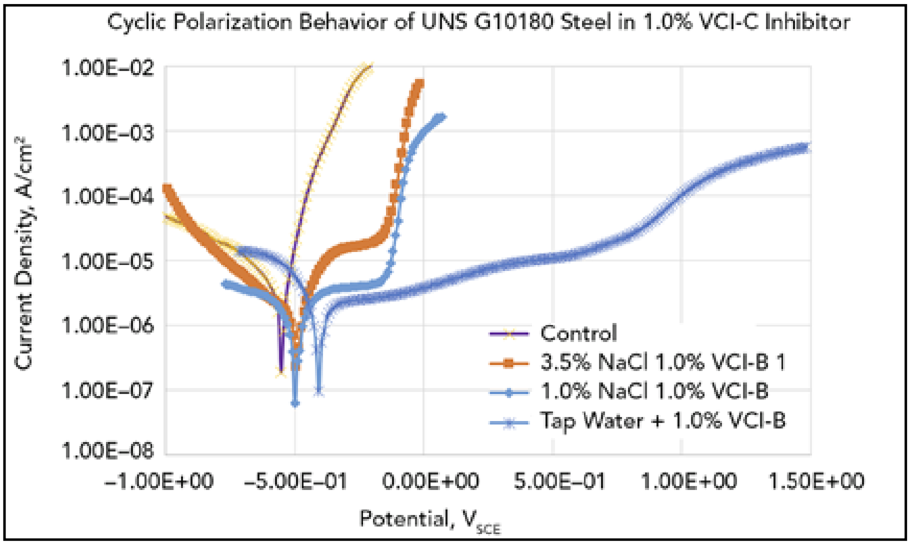

FIGURE 3 Cyclic polarization behavior of UNS G10180 steel in 1.0% VCI-C at different aqueous solutions.

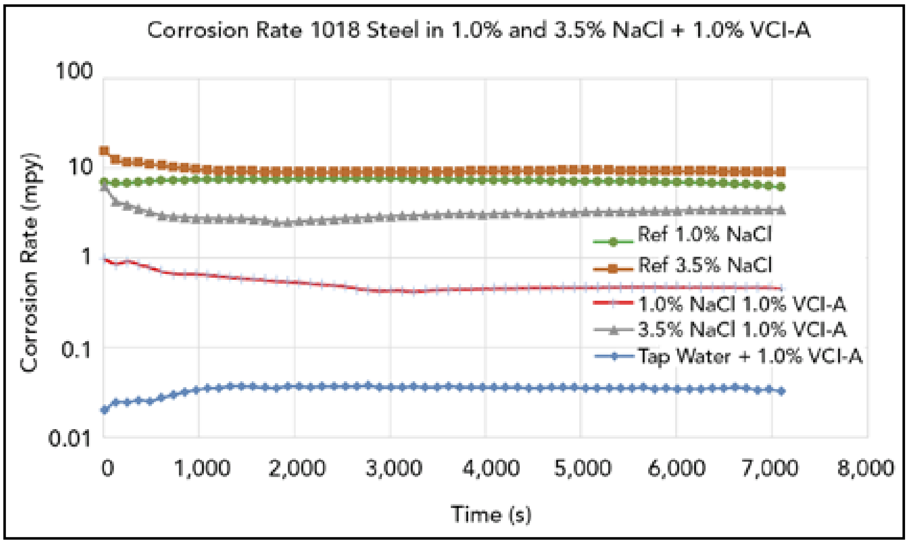

FIGURE 4 Corrosion rate measurement (based on linear polarization resistance [LPR]) of UNS G10180 steel in 1.0% VCI-A at different aqueous solutions.

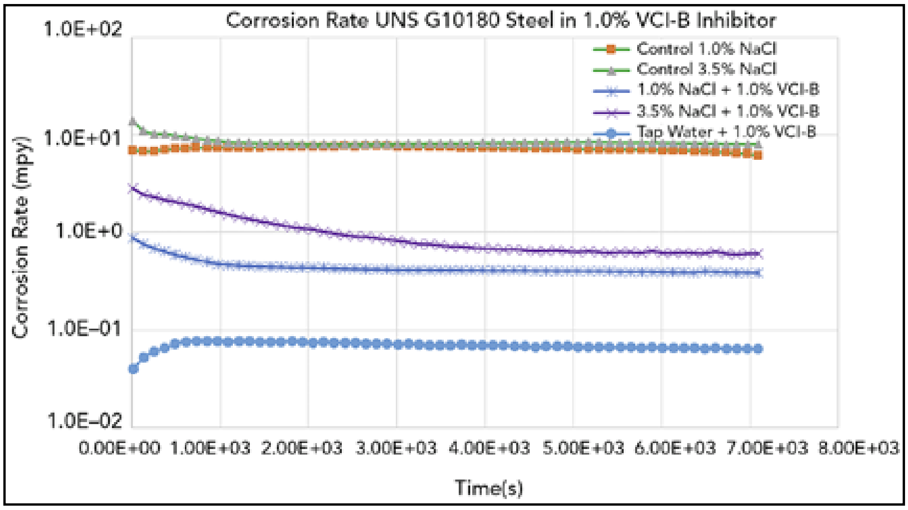

FIGURE 5 Corrosion rate measurement (based on LPR) of UNS G10180 steel in 1.0% VCI-B at different aqueous solutions.

Experimental Procedure

The main objective of this investigation was to study corrosion behavior of steel samples used as base material for pipelines to demonstrate effective corrosion protection of different VCIs. The choice of corrosion inhibitors for this study was made based on their functions and effectiveness in different aqueous solutions. VCI-A, VCI-B, and VCI-C are water-soluble products that have been demonstrated to inhibit corrosion of low carbon steel (CS) during hydrotests using fresh water. These inhibitors are a combination of film formers and VCIs. The main ingredients are salts of amines, organic acids of different chemical structures, and triazole. The main function of these products is to form a protective film with some VCI action. All these inhibitors are biodegradable and are surface modifiers.

The steel used in this study was a low CS with a chemical composition (wt%) of 0.14 to 0.22% C, 0.3 to 0.65% Mn, ≤0.3% Si, ≤0.05% S, ≤0.045% P, and the remainder Fe. The CS samples were pretreated prior to the experiments by polishing with silicon carbide paper (240, 320, 400, 600, and fine polishing with 1.0 µm almina powder), degreased in acetone for 5 min in an ultrasonic bath, then rinsed with ethyl alcohol and dried in a desiccator at room temperature. The three different USDA bio-based inhibitors labeled VCI-A, VCI-B, and VCI-C were remixed with different dosages (0.5% or 1.0%) in order to find out the optimum proportional relation for effective protection. The salt solutions were prepared based on 1.0% NaCl or 3.5% NaCl solutions. The corrosion behavior of the low CS was investigated when exposed to three different corrosion inhibitors in salt solutions using electrochemical techniques, total immersion tests, and vapor-inhibiting ability (VIA) (NACE TM0208-201811). Electrochemical polarization standards per ASTM G61[12] (cyclic polarization), polarization resistance and corrosion rate measurements, and electrochemical impedance spectroscopic (EIS) techniques were used to evaluate the behavior of these inhibitors on the different alloys in different chloride solutions.

The corrosion behavior of low CS was investigated using EIS in different salt concentrations. The experiments were conducted using commercially available systems for EIS and direct current corrosion tests. Bode plots were created from the data obtained using the potentiostatic technique. By comparing the Bode plots, changes in the slopes of the curves were monitored as a means of establishing a trend in the R_p value over time. To verify this analysis, the R_p values were also estimated by using a curve fitting algorithm on the Nyquist and Bode plots. In these plots, the R_p and RΩ combined values are displayed in the low frequency range of the Bode plot and the RΩ value can be seen in the high frequency range of the Bode plot. The diameter of the Nyquist plot is a measure of the R_p value. During this investigation, changes in the polarization resistance (R_p) of these alloys were monitored to ascertain the degree of effectiveness for these inhibitors to lower the corrosion rate.

The NACE TM0208-2018 Standard Test Method was also used to evaluate the VIA of various forms of VCI.[11] This laboratory test method evaluates the VIA of various forms of VCI materials for temporary corrosion protection of ferrous metal surfaces. The VIA corrosion test method represents standard conditions in a test jar of water-saturated warm air without the presence of accelerating contaminants. The combination of (1) vapor transport across a gap containing

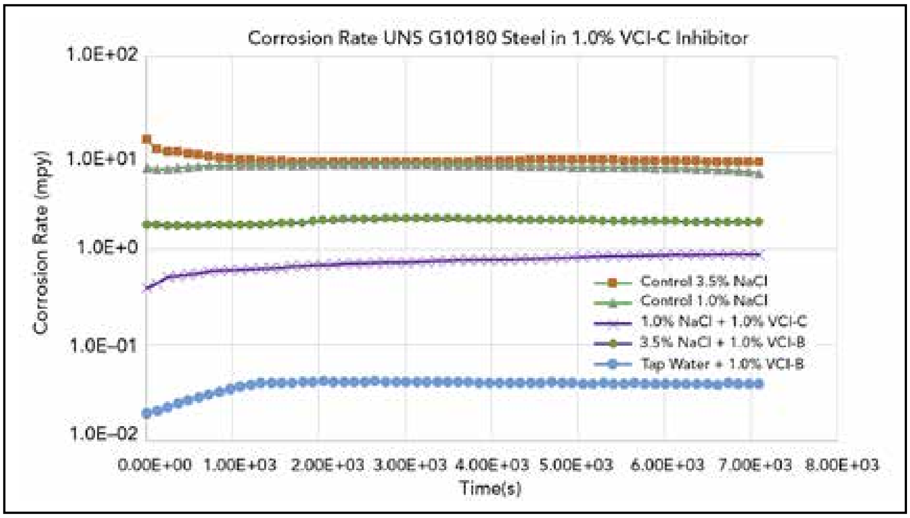

FIGURE 6 Corrosion rate measurement (based on LPR) of UNS G10180 steel in 1.0% VCI-C at different aqueous solutions.

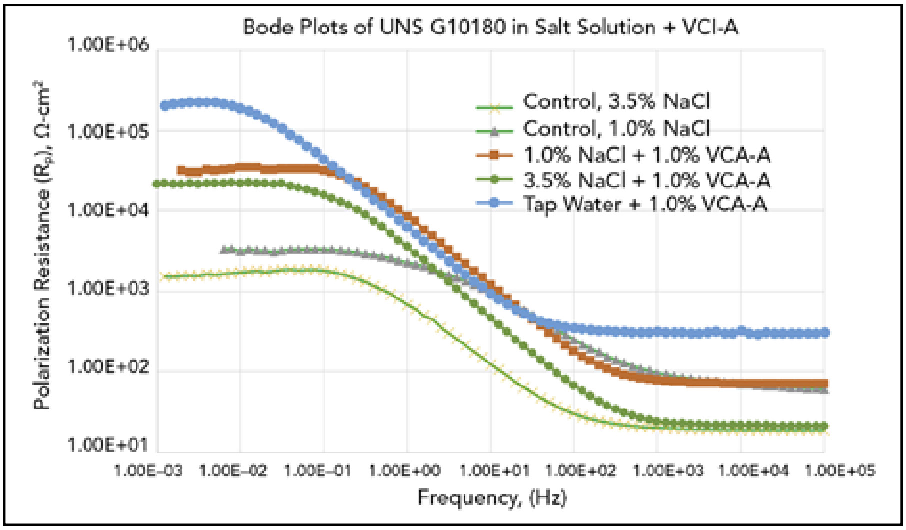

FIGURE 7 EIS Bode plot of UNS G10180 steel in 1.0% VCI-A at different aqueous solutions.

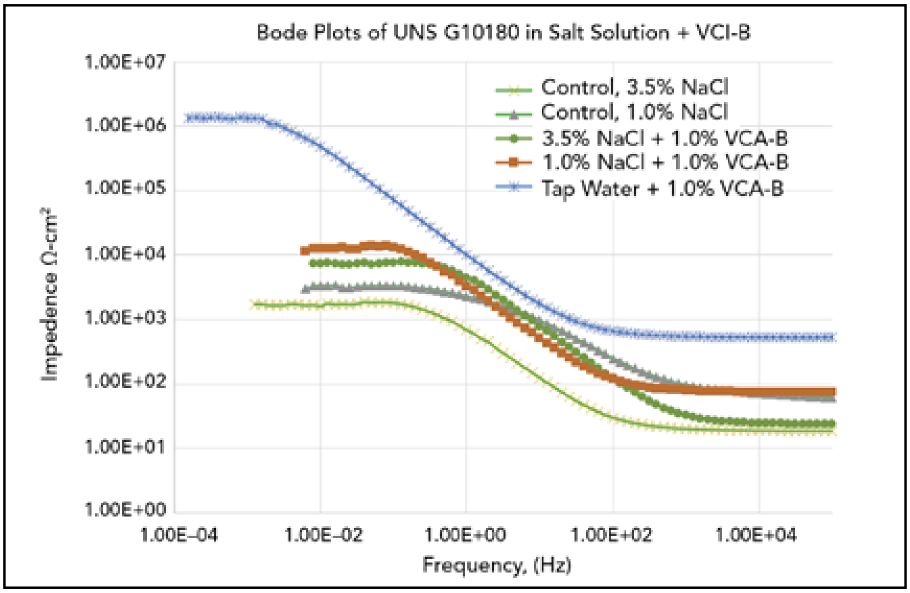

FIGURE 8 EIS Bode plot of UNS G10180 steel in 1.0% VCI-B at different aqueous solutions.

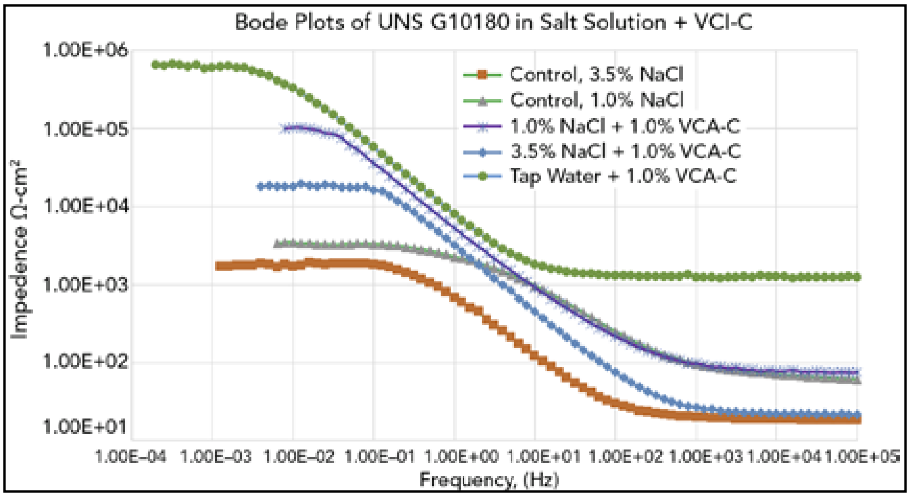

FIGURE 9 EIS Bode plot of UNS G10180 steel in 1.0% VCI-C at different aqueous solutions.

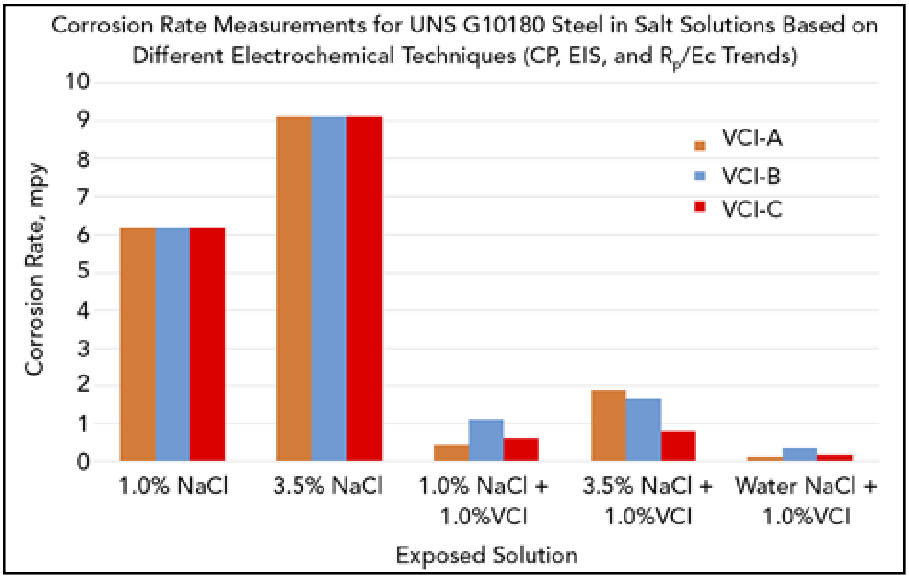

FIGURE 10 Corrosion rate measurements of UNS G10180 steel using different electrochemical techniques (cathodic protection, EIS, and Rp/Ec trends) at different aqueous solutions.

air, water vapor, and VCI, and (2) corrosion protection are evaluated in this test method. The VIA tests consist of four steps of sample conditioning or saturation for 20 h at 22 °C, a cooling cycle at 2 °C, and prewarming at 50 °C, followed by 3 h at 22 °C for specimen conditioning. After the last 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 inserted sensors and data logging software. Post-test evaluation of the surface condition of exposed samples involved digital light microscopy, scanning electron microscopy (SEM), energy dispersive spectroscopy, and x-ray photoelectron spectroscopy.

Results and Discussion

Figures 1 to 3 show the polarization behavior for UNS G10180 steel in 1.0% inhibitor (different VCI products) in different salt solutions. The most noticeable changes are the positive shift in the breakdown potential and expansion of the passive range for these alloys when inhibitors were added. These inhibitors acted as effective cathodic inhibitors. The inhibitor changed the reactivity by reducing the pH level, increased the passivation range significantly, and was beneficial in reducing localized corrosion damages. As demonstrated in these polarization curves, extension of the passive zone contributes to the stability of the protective oxide film over a wider electrochemical range, resulting in a more stable passive film, and shifts the critical pitting potential to higher levels.

Corrosion rate measurements based on the linear polarization rate are shown in Figures 4 to 6. The effectiveness of these VCI products is confirmed in various water chemistries including fresh and salt water. The corrosion rate dropped from ~10 mpy for the salt solution to less than 1 to 2 mpy when various inhibitors were added. The effectiveness of these inhibitors was remarkable in the fresh water (less than 0.4 mpy).

The corrosion behavior of low CS was investigated using EIS in different salt concentrations. Various Bode plots are shown in Figures 7 to 9. These results showed a significant increase in polarization resistance when inhibitors were added. Measured polarization resistance jumped from 2,000 to 3,000 Ω-cm^2 to more than 30,000 to 110,000 Ω-cm^2. These increases in polarization resistance are equivalent to a significant decrease in the corrosion rate.

Figure 10 summarizes the average measured corrosion rate by different electrochemical techniques. These results reaffirmed the necessity to add these inhibitors to testing media during hydrotesting.

The laboratory test method evaluations of the VIA of these VCI products are shown in Figures 11 to 12. Samples were visually inspected and their surface conditions were documented after VIA tests were completed using optical digital microscopy and SEM. Based on three sets of VIA tests, the observation showed that the control had a Grade 0 (severe pitting corrosion), while the addition of VCI-A, VCI-B, and VCI-C resulted in a significant improvement to Grade 3 (almost no corrosion attacks). These results showed that these inhibitors have a very strong VIA. Additionally, any leftover residue of hydrotesting solution in pipes will be beneficial and provide extra protection during a storage period, contrary to the stagnant wet condition that testing without an inhibitor might cause.

The VIA visual observations are shown in Figure 11. Figure 12 shows SEM micrographs of the steel sample after VIA tests. The high-resolution SEM images show a significant improvement for VCI-A, VCI-B, and VCI-C with no sign of any pitting corrosion.

Figure 13 shows the effects of different corrosion inhibitors on the mechanical behavior of low CS. Tensile tests on the exposed samples after four-week immersion tests indicated that the level of corrosion attacks were minimized, and no sign of any deterioration in ductility of the exposed samples was detected.

Inhibitor Adsorption Mechanism

The adsorption isotherm relationship between surface coverage and temperature for the VCI-A, VCI-B, and VCI-C inhibitors on the surface of steel is shown in Figure 14. Adsorption energy was –21,520 J/mol for VCI-A, –22,950 J/mol for VCI-B, and roughly –24,970 J/mol for VCI-C. This energy range is indicative of a good physical adsorption to the metal surface. Generally a multilayer adsorption energy between –5,000 to –50,000 J/mol is defined as a physisorption mechanism, a weak, long-range bonding. However, it can be seen that the interaction of VCI-C with the steel surface is higher than the other inhibitors, leading to better corrosion protection. XPS depth profiling analysis showed ~60 to 65 nm of adsorbed inhibitor on the exposed samples, indicating multilayer adsorption of inhibitor molecules to the steel surfaces. Therefore, the Brunauer Emmett Teller Model (BET Model) is a more realistic adsorption model than the monolayer Langmuir model for this case.[13-15] But for the adhesion energy calculation between inhibitor molecules and the metal surface, it is appropriate to use the monolayer Langmuir model.[16]

Conclusions

This investigation demonstrated that VCI additives can prevent corrosion of CS during and after hydrotesting. When necessary, other VCI products can complement hydrotest additives for long-term storage. Electrochemical cyclic polarization showed formation of a stale passive range when these inhibitors were added to the environments.

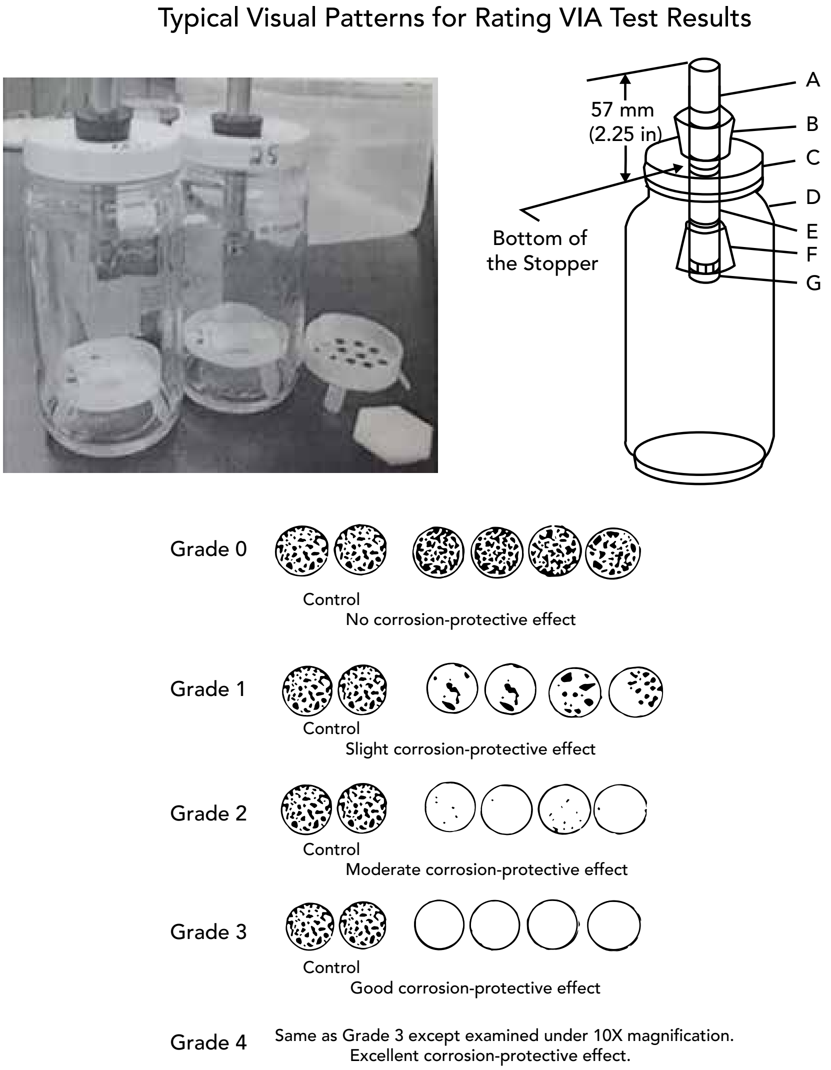

FIGURE 11 **Test setup and rating criteria for the NACE TM0208-2018 Standard Test Method.**

The effectiveness of VCI products is confirmed in various water chemistries including fresh and salt water. The corrosion rate dropped from ~10 mpy for the salt solution to less than 1 to 2 mpy when various inhibitors were added. The effectiveness of these inhibitors was remarkable in fresh water (less than 0.4 mpy).

Tensile post-immersion tests did not show any loss in mechanical properties of the exposed samples. Both strength and ductility of the low CS samples were maintained. Adsorption energy was about –21,520 J/mol for VCI-A, –22,950 J/mol for VCI-B, and roughly –24,970 J/mol for VCI-C, indicating a strong physisorption mechanism (Figure 15).

Results indicated that these bio-based, environmentally friendly VCI additives have low toxicity levels and waters containing these VCI products remain safe for many species, allowing discharge according to local specifications.

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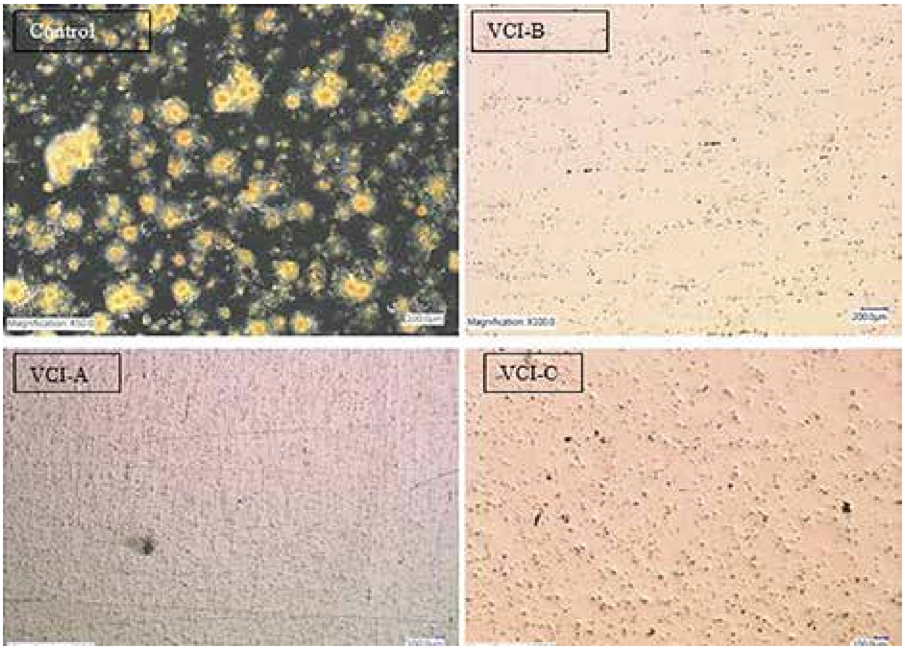

FIGURE 12 Optical micrographs of the steel sample after VIA tests. These tests showed a significant improvement for VCI A, VCI-B, and VCI-C compared with the control sample. VIA rating: Control Grade 0; VCI-A, VCI-B, and VCI-C Grade 3.

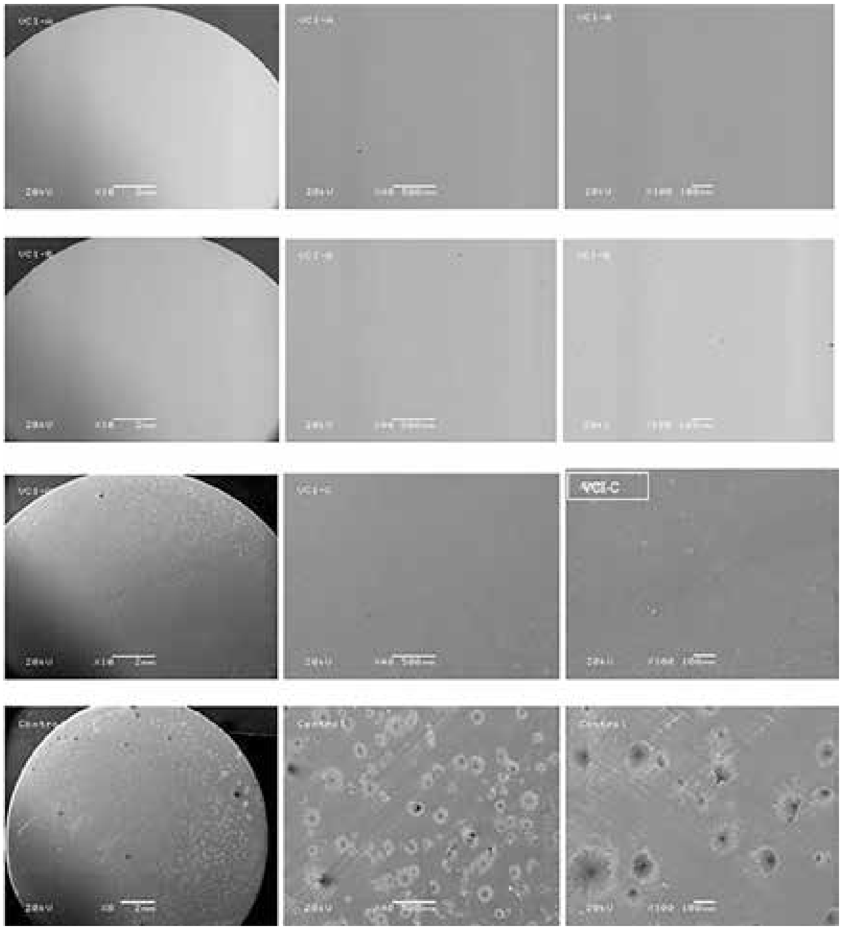

FIGURE 13 SEM micrographs of steel samples after VIA tests. Superior performance for VCI-A, VCI-B, and VCI-C were observed compared with the control sample. VIA Rating: Control Grade 0; VCI-A, VCI-B, and VCI-C Grade 3.

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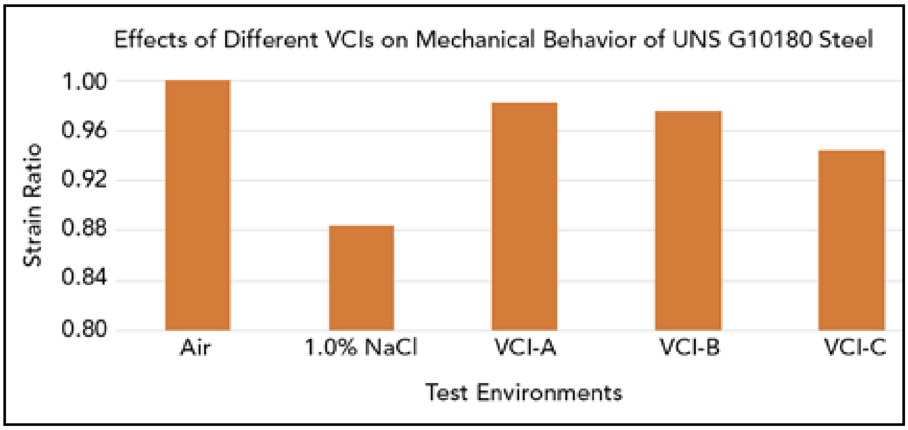

FIGURE 14 Effects of different inhibitors on tensile ductility of UNS G10180 steel.

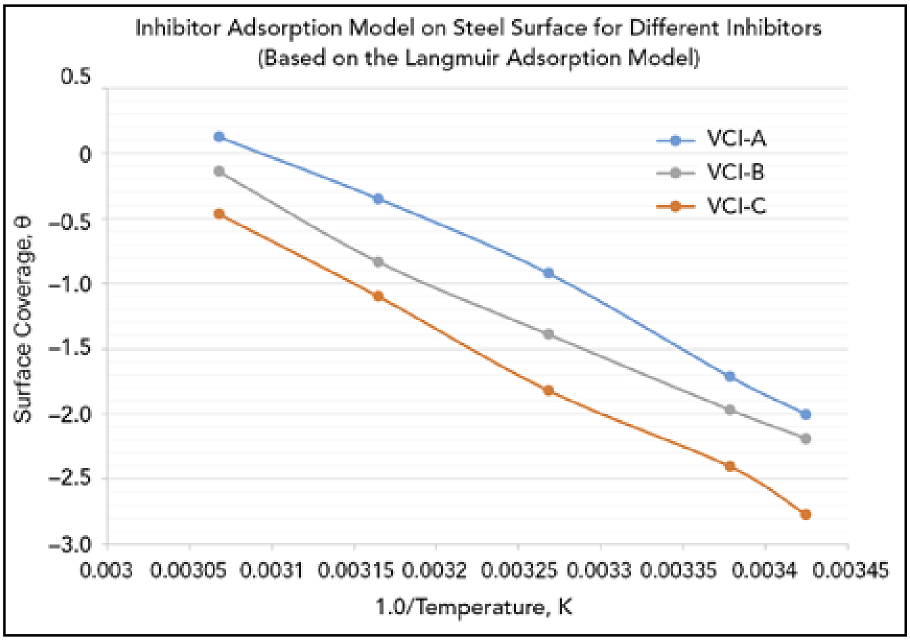

FIGURE 15 The adsorption isotherm relationship between surface coverage and temperature for different VCIs on the surface of steel. Adsorption energy was roughly –21,500 to –24,970 J/mol for these inhibitors.

Use of Volatile Corrosion Inhibitors in Packaging to Protect Equipment from Corrosion

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Understanding environmental conditions experienced during shipping (both domestic and export) and/or storage is critical when determining the most effective corrosion control system for metal components. Temperature and humidity sensors were used to help understand the conditions within industrial packaging applications, during different overseas shipping routes, and during subsequent warehouse storage. The effect of secondary packaging (i.e., polyethylene film) on temperature and humidity within a package was also evaluated. The scope of this article is to compile and analyze the data, and utilize it to help develop the best corrosion prevention strategies.

Quantifying environmental conditions experienced during shipment and storage of various metal components provides critical data, with respect to choosing the most effective preservation system. Differences in conditions can be seen as a shipment moves from port to open water, from a heated warehouse to an unheated truck, and also from the outside of the pack to the inside (i.e., box, crate, or within a piece of equipment). Analyses were made to evaluate these scenarios. Differences were evaluated inside the packaging systems, as well as from the outside to the inside of a system. These were used to gain insight into the efficacy of various corrosion-inhibiting systems, as well as the efficacy of adding a volatile corrosion inhibitor (VCI) to a given system.

Laboratory Testing

Accelerated corrosion testing was performed for spare gear components used by a heavy equipment original equipment manufacturer (OEM), in preparation for a plant shutdown. The goal of this testing was to determine the efficacy of various packaging systems, while trying to also understand environmental conditions experienced within a given pack. The OEM wanted to be able to monitor conditions within its warehouse, and subsequently within each pack, in real time, over the course of the shutdown.

Gear components were wrapped in systems meant to simulate those used for shipment and storage. Temperature and humidity sensors were added to each pack, to quantify the effect of packing with a 50-µm VCI polyethylene (PE) bag. All systems were then exposed to modified ASTM D1748[1] testing conditions for 185 h.

Overseas Shipping

Environmental conditions during an overseas shipment can shift dramatically, from leaving port to crossing the equator. The daily rise and fall of temperature and humidity may not be as dramatic, but the overall trip from one side of the world to the other provides continuous challenges for nearly every industry. In this application, temperature and humidity sensors were placed inside two packages to evaluate the effect of differing packaging systems to control temperature and humidity swings within a cardboard container shipping components from the United States to China.

A second overseas shipping application examined the efficacy of VCI in protecting the internals of a steel fuel tank. The equipment OEM had been experiencing corrosion issues during this shipment, due to the severe conditions experienced both during the shipment, and subsequent (indefinite) outdoor storage. Crawler units were sent from the United States to Brazil to compare treated and untreated fuel tanks. Temperature and humidity sensors were placed both inside the tank and to the frame of the crawler to measure the conditions experienced during shipment. Upon receipt, the tanks were opened and inspected for corrosion, to determine the efficacy of the VCI additive, and the sensors were recovered to review environmental data.

Experimental Procedure

Laboratory Testing—Modified ASTM D1748

Test standard ASTM D1748 creates an accelerated corrosion atmosphere by combining high heat (48.9 +/−1.1 °C [120 +/−2 °F]) with constant condensing humidity and a steady rotation of test samples at ~0.33 rpm. Testing is performed for a predetermined period, or until such time that corrosion is observed on the metal surface.

In this evaluation, ASTM D1748 conditions were achieved with respect to temperature and humidity. However, due to the size and configuration of test parts and packaging, testing in true ASTM D1748 conditions was not feasible.

The goal of this test was twofold. The first goal was to evaluate the packaging system used for storage of component parts at the warehouse of a heavy equipment OEM. The existing packaging system was as follows:

- Sheet of plywood placed on a pallet
- Sheet of VCI paper on top of the plywood
- Layer of machined metal parts on the VCI paper

- Second layer of VCI paper on top of the metal parts
- Second piece of plywood

This system was repeated for multiple layers, at which point the entire pallet was wrapped in non-VCI stretch wrap.

For comparison, the corrosion-inhibiting efficacy of a 50-µm VCI PE bag was evaluated. This bag would simulate a large over bag, serve as a pallet liner, and separate the metal part and VCI paper from the plywood. Specifically, the test system was as follows:

- Sheet of plywood
- VCI bag (bottom)
- VCI paper
- Metal part
- VCI paper
- VCI bag (top, folded over and closed, not heat-sealed or taped)
- Sheet of plywood
- Non-VCI PE stretch wrap

This system was compared to the current control system, as previously described, with a single gear component in each pack (Figure 1).

The second goal of the test was to track differences in temperature and humidity within the control pack vs. the pack with the 50-µm VCI PE over bag. To accomplish this goal, temperature/relative humidity (RH) sensors were placed inside both packs during testing. Testing was run for 185 h, at which point the gear components were unwrapped, visually inspected, and photographed. Temperature and RH data were also collected from the sensors placed within the respective packs.

Real World Analysis— Ocean Shipments

The first real world analysis involved a shipment of metal components from Illinois, United States to China. The process involved packing machined parts in small boxes. Each box was lined with 50-µm non-VCI PE film, and within this film, parts were wrapped in VCI paper. Boxes were then bulk packed onto a pallet. The entire pallet of boxes would then be enclosed with a non-VCI PE shrink film. This system was compared to a second, less labor-intensive system, whereby the boxes were lined with VCI barrier paper, but no secondary bag. The entire pallet was covered with a non-VCI PE bag. Within each pack, a temperature and humidity sensor was placed in one box (Figure 2). Conditions were logged for the duration of the 51-day shipment process.

The second real world analysis involved evaluating temperature and humidity conditions experienced by crawler units shipped from Iowa, United States to Brazil. Two temperature and humidity sensors were placed on the crawler; one attached to a modified fuel cap, and a second attached to a hose on the vehicle exterior. The first sensor allowed for measurement of conditions experienced inside a partially filled biodiesel fuel tank, where the end user had been experiencing repeated corrosion problems during overseas shipment. Two crawlers were sent; one with standard biodiesel fuel, and the second

FIGURE 1 Wrapped gear component prior to testing.

FIGURE 2 Boxed parts prior to shipment, with sensor in place.

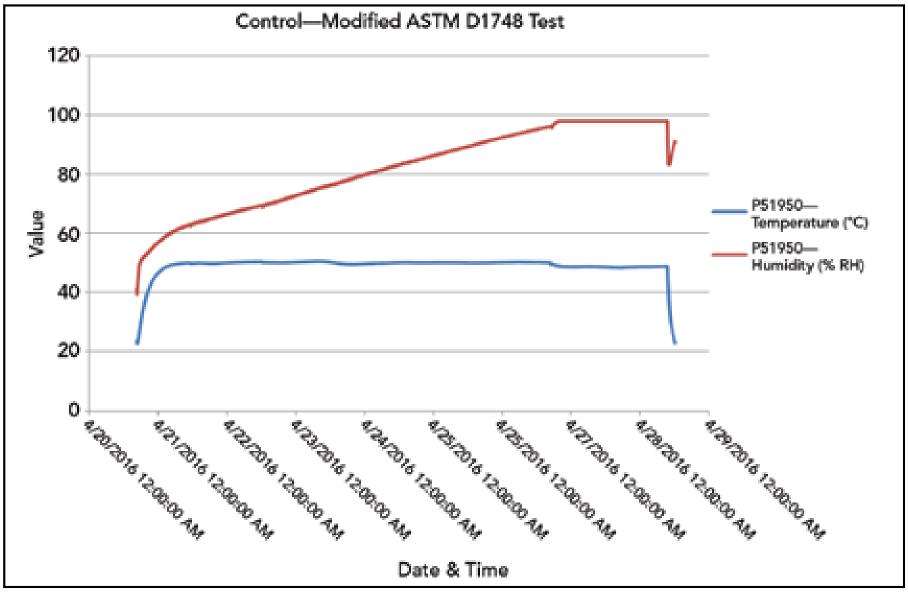

FIGURE 3 Temperature and RH data from the control pack. In this pack, temperature reached 50 °C within 16 h. RH reached 75% in 62 h, and eventually reached 98%, where it remained for the final 36 h of testing.

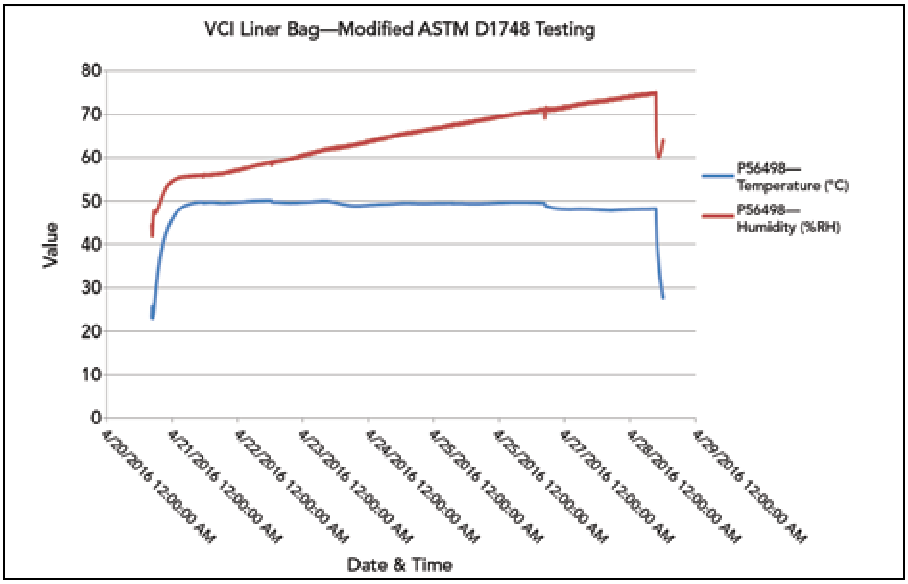

FIGURE 4 Temperature and RH data from the pack with 50-µm VCI PE liner bag. Temperature reached 50 °C after 36 h, while RH reached a high of 75% at the end of testing.

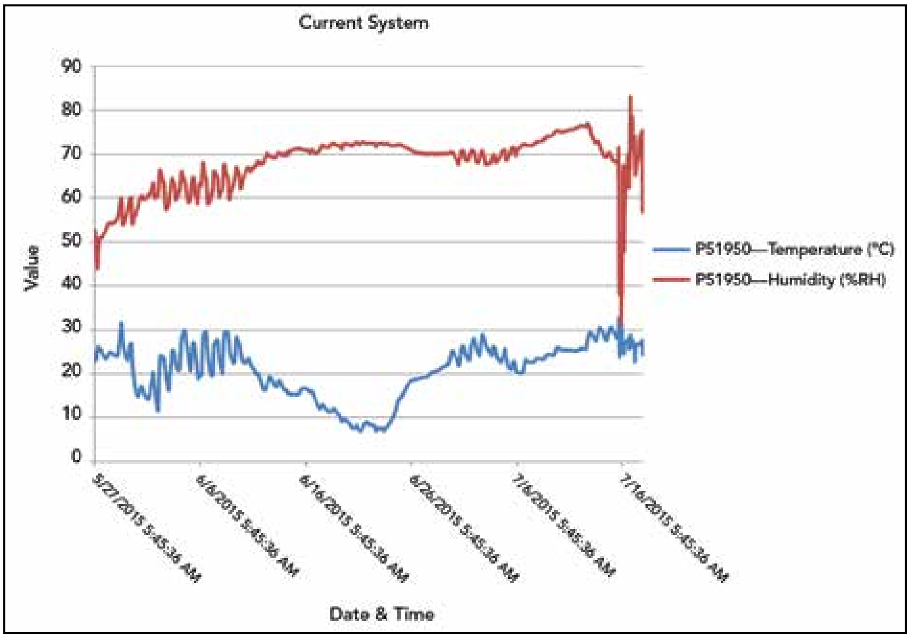

FIGURE 5 Sensor data from an overseas shipment, United States to China. The data above were the conditions within the control (current) end user system.

with a VCI additive (0.5% by tank volume) in the biodiesel. In addition to evaluating the conditions experienced in this shipment, the efficacy of the VCI additive was evaluated. It should be noted that only two sensors were available for this test. As such, both sensors were on/in the VCI-treated crawler.

Results

Laboratory Testing—Modified ASTM D1748

After 185 h of testing, the control part showed significant corrosion, while the part packed with a 50-µm VCI PE liner bag showed no corrosion.

When temperature and humidity data were reviewed, it was shown that both temperature and humidity increases were significantly slowed inside the pack with the 50-µm VCI PE over bag. Whereas the internals of the control pack took 16 h to reach external testing conditions of 50 °C (Figure 3), the second pack took 36 h to reach 50 °C (Figure 4). When reviewing RH, the control pack reached 75% RH after 62 h of testing, and eventually reached 98%, where it remained for the final 36 h of testing. Conversely, the pack with 50-µm VCI PE over bag reached a high RH of 75% at the end of testing.

Real World Analysis—Overseas Shipment 1

Average RH within the shrink-wrapped pallet was 68%, compared to 59% for the PE liner/bag covered pallet. The control pack exceeded 60% RH within four days, compared to 31 days for the PE liner/bag + VCI barrier paper system. Near the middle of the shipment, temperature dropped from 25 °C to 9 °C. During this time, the RH within the shrink-wrapped pallet did not change significantly (Figure 5). Conversely, changes in RH within the second pack closely followed temperature changes during this time, and throughout the rest of the shipment (Figure 6). This suggests that the individual PE bag may be trapping moisture inside. Corrosion was not seen in parts from either packaging system during this evaluation.

Real World Analysis—Overseas Shipment 2

The two crawlers were shipped from Iowa, United States on September 2, 2016. They were sailed from port on September 6, 2016, at which point all readings showed daily fluctuations. The internal (fuel tank) sensor showed these fluctuations until September 16, whereas the external sensor continued to show fluctuations until September 21. Both crawlers arrived in Brazil on September 29, 2016. Initial inspection took place on October 20, 2016, at which time sensors were sent back to the United States for data collection. The external conditions continued to fluctuate during this time, whereas the internal readings stayed consistent until a few days before initial inspection.

Additionally, corrosion was found in the fill neck of the untreated tank upon receipt inspection. In the tank treated with VCI, no corrosion was found. For the purposes of this evaluation, exterior surface corrosion was not monitored.

Conclusions

Use of temperature and humidity sensors can provide information critical to determining the most effective packaging and preservation methods for numerous storage and shipping applications.

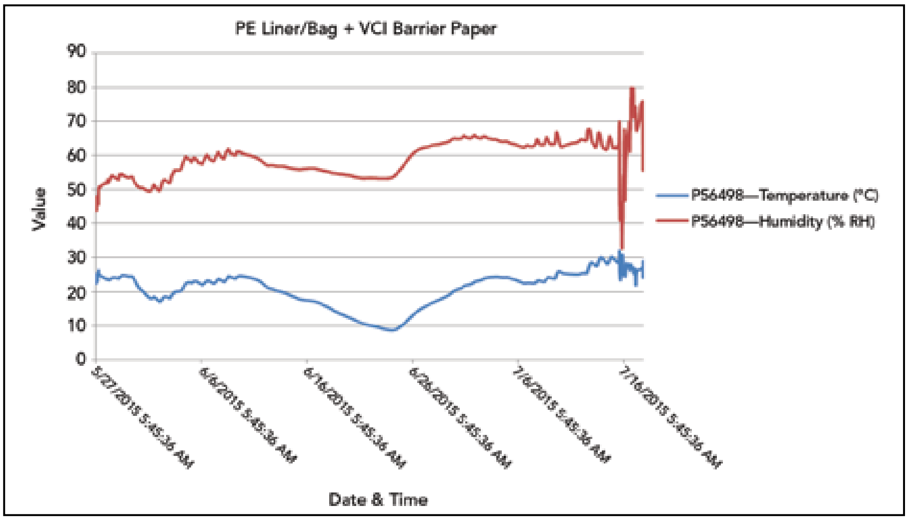

FIGURE 6 Sensor data from an overseas shipment, United States to China. The data above were the conditions within a packaging system utilizing a PE liner and bag, plus VCI barrier paper.

FIGURE 7 VCI-treated fuel tank after shipment. No corrosion was visible.

Laboratory testing, utilizing Modified ASTM D1748 conditions, showed that the use of a 50-µm VCI PE liner bag reduced the RH inside a package by 23% after 185 h, from 98% to 75%. Further, a time to temperature increase to 50 °C inside the pack was slowed by more than 100%, from 16 h in the control pack to 36 h in the pack with an additional liner bag. This system also showed increased corrosion protection, compared to the control system, which only utilized VCI paper, stressing the importance of considering secondary VCI protection in some applications.

Two overseas shipments brought a variety of results. The first showed a significant reduction in RH exposure within a packaging system that utilized a combination of VCI barrier paper inside each box, non-VCI PE pallet liner, and over bag. This was compared to a control system where parts were wrapped in VCI paper and non-VCI PE bags in each box and the entire pallet being wrapped with PE shrink film. Although temperatures were constant among the two packs, the control pack reached and sustained an RH of 60% or greater within four days of shipment, compared to 31 days for the second pack. While corrosion was not seen in either of the tested packaging systems, the revised method would be less time-consuming and more cost effective. VCI paper would continue to be used, while eliminating the need for adding a PE bag to every individual box, and not requiring heat shrinking for every pallet.

The second overseas shipment explored differences in conditions experienced outside a large crawler unit, compared to conditions inside the fuel tank. Sensor readings showed that conditions on the vehicle exterior are much more severe, and also much more volatile, compared to inside the fuel tank. However, conditions within the fuel tank were still severe enough to induce corrosion during a six-week shipment and storage period, as seen in the untreated biodiesel tank. Conversely, a tank treated with VCI additive did not show any corrosion during this time (Figure 7). This fuel tank corrosion was the biggest concern of the end user, and combining the success of a VCI additive with the quantitative environmental data led to a change in preservation process prior to shipment.

Acknowledgments

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Corrosion Protection in an Oil System with Water Ingress by Use of Volatile Corrosion Inhibitors

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Volatile corrosion inhibitors (VCIs) are commonly used in various oil systems to prevent corrosion during preservation and in intermittent operation. However, water ingress still introduces the risk of corrosion when water separates and pools at the bottom of these systems. Traditional corrosion inhibitors used in lubricating oils provide good corrosion protection in the oil phase, but cannot offer protection beneath the oil-water phase line due to their typical hydrophobic nature. It has been determined that the use of proper organic VCIs (which also offer protection in the vapor phase and oil phase) can partition into the water phase and provide additional corrosion protection even in the case of water contamination.

Water handling is an important property for lubricating oils in many applications. Even small amounts of water can cause serious damage in a system, decreasing the oxidative stability of the oil, increasing deposition and contaminants, and reducing the performance of additives.[1] In storage and lay-up, the presence of water can promote surface corrosion on key components inside the system. Over time, each of these factors contributes to shortening equipment life. While operating oils may be replaced, oxidation on metal surfaces may result in costlier and time-consuming repairs.

Studies and laboratory experiments have previously investigated the effectiveness of oil-soluble/water-dispersible corrosion inhibitors to partition into brine and provide protection to pipeline systems.[2] However, key features of these experiments and the application of these inhibitors is their continuous application into flowing/operating systems. Even traditional efficacy tests of these types of inhibitors, such as the continuous wheel test, investigate inhibitor performance under sheer conditions.[3] This opportunity of mixing dispersion is not offered in stagnant preserved systems where water ingress is slow and inconsistent.

Amine-based inhibitors, including imidizolines and aminocarboxylic acids, have been explored for petroleum industries. Inhibitors are carefully crafted to balance a variety of properties for varying systems.[4] Inhibitors for preservation and stagnant applications must be carefully chosen based on the desire for solubility in both oil and aqueous systems.

The use of a specific oil-based corrosion inhibitor additive, with the ability to passively partition from the oil phase into the aqueous phase, is investigated here. The effectiveness of partitioning (at various concentrations of corrosion inhibitor in the preservation oil) is evaluated by analyzing the concentration of the nitrogen-based corrosion inhibitors in the aqueous phase through the Kjeldahl Method for determination of organic nitrogen.[5] The corrosion protection capabilities of the partitioned corrosion inhibitor is quantified and compared at various concentrations using increasingly rigorous iterations of immersion corrosion testing (modeled after ASTM G31[6]) and electrochemical impedance spectroscopy (EIS).

Experimental Procedure

The evaluation of the corrosion protection provided by a partitioned inhibitor required several different steps. Testing was performed to evaluate the amount of inhibitor that will partition into the aqueous phase under varying circumstances, as well as two separate methods to assess the degree of corrosion protection provided.

Extraction of Corrosion Inhibitor from VCI Oil Additive

DETERMINATION OF OIL/WATER RATIO

A common practice for preservation of oil systems includes filling the system with standard lubricating oil treated with a compatible VCI additive. According to the manufacturer's recommendations, VCI oil additives are dosed at 3 to 5% by volume of the base oil inside the system. Other recommendations include directly fogging the VCI oil additive into the preserved system at a specified dosage per volume of the oil system. The amount of VCI additive inside the system will affect the partitioning of the corrosion inhibitor into the aqueous phase. Several ratios of oil phase to water were examined to investigate the partitioning behavior of the corrosion inhibitor. At recommended dosages of 3 to 5%, the partitioning effect of the corrosion inhibitor from the VCI additive will be evaluated with the neat additive and with the additive dosed as recommended by the manufacturer. The ratio of oil phase to aqueous phase was varied as well, investigating 1:1 and 9:1 ratios of oil to water.

TABLE 1 Sample Identification for VCI Oil Additive Extraction

Sample No.	VCI Oil Additive Concentration (%)	Oil to Water Ratio	Ratio of VCI Additive to Water
1	100	1:1	1:1
2	100	9:1	9:1
3	5	1:1	0.05:1
4	5	9:1	0.45:1

Extraction of Corrosion Inhibitor

A solution of 5% VCI oil additive in standard synthetic poly alpha olefin oil was created. Along with the concentrated oil additive, Table 1 shows the solutions made.

Oil solutions were added to a large beaker and deionized (DI) water was gently poured through the oil layer until the desired oil to water ratio was achieved. Each beaker was covered and allowed to sit for 24 h. After the 24-h period, the oil layer was decanted and separated using a separatory funnel. The remaining aqueous phase was collected, labeled, and submitted for analysis. A sample of the DI water was also submitted for testing to ensure no base level of organic nitrogen is present in the solvent.

Because the volume of water ingress in a preserved system would generally be low compared to the volume of the treated oil, Sample No. 4 is considered the most representative of a real-life preservation system. For preserved systems when the VCI oil additive is fogged and water ingress is experienced, Sample No. 1 could be considered the most representative test sample for the system.

Determination of Corrosion Inhibitor Concentration

The primary corrosion inhibitor component identified in the VCI oil additive is an organic nitrogen-based corrosion inhibitor compound. Aqueous samples were sent to a third-party analytical laboratory for analysis using the Kjeldahl Method for determining organic nitrogen content in aqueous solutions.

Immersion Corrosion Testing

Two sets of immersion corrosion testing were performed as part of this evaluation. The first evaluation was performed with no duplicates and panel cleaning was performed with 1% hydrochloric acid (HCl), 1% commercial acid corrosion inhibitor, and 98% DI water mixture. The second evaluation was performed in triplicate and panel cleaning was performed with a standard ASTM G01[7] solution.

Immersion Corrosion Testing—First Iteration

Testing was performed in DI water, with varying amounts of the corrosion inhibitor identified above from the VCI oil additive in solution. The solution was held in a cylindrical glass cell with a 5-in (127-mm) height and 2-in (50.8-mm) diameter. Two hundred g of each solution were used in each test cell to ensure full immersion of the tested panels (0.63 by 1 by 3-in [16 by 25.4 by 76.2-mm] SAE 1008/1010 cold-rolled steel). Panels were prepared by hand polishing both faces to a consistent finish with 240 grit aluminum oxide (Al_2O_3) abrasive paper. Panels were cleaned with methanol, weighed to the nearest 0.1 mg, and placed into the respective solutions. Test cells were placed into a 40 ± 2 °C oven for approximately three weeks. At this time, panels were removed, rinsed with methanol, and oxides were removed from the surface via a 1% concentrated HCl solution, also containing 1% corrosion inhibitor to prevent flash corrosion during the cleaning process. The panels were examined for mass loss and the rate of corrosion was calculated using the following formula from ASTM G31 (Equation [2], Section 12.4):

$$\textit{Corrosion Rate (mpy)} = \frac{3.45\times10^{6}\times W}{A\times T\times D} \qquad (1)$$

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 1008/1010 steel). The corrosion rate reduction was also calculated by comparing the control sample to the test samples with the following formula:

$$\textit{Corrosion Rate Reduction} = \left(1-\frac{R}{C}\right)\times100\% \qquad (2)$$

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

A single panel was prepared for each tested solution, along with a single panel to be tested in DI water as a control. A single prepared, but untested, steel panel was subjected to the cleaning procedure as above. The mass loss of the cleaning procedure was determined, and this mass loss was subtracted from the mass loss measured in each tested panel, in order to determine the true mass loss from the immersion corrosion testing.

Immersion Corrosion Testing—Second Iteration

Testing was performed in DI water, with varying amounts of the corrosion inhibitor identified above from the VCI oil additive in solution. The solution was held in a cylindrical glass cell with a 5-in height and 2-in diameter. Two hundred g of each solution was used in each test cell to ensure full immersion of the tested panels (0.63 by 1 by 3-in SAE 1008/1010 cold-rolled steel). Panels were prepared by hand polishing both faces to a consistent finish with 240 grit

TABLE 2 Corrosion Inhibitor Content Results

Sample No.	Ratio of VCI Additive to Water	Inhibitor Detected (ppm)
1	1:1	1,368
2	9:1	2,234
3	0.05:1	535
4	0.45:1	802

TABLE 3 Concentration of Corrosion Inhibitor in Tested Solutions

Sample Label	Inhibitor Concentration (% by weight)	Inhibitor Concentration (ppm)
Control	0	0
A	0.5	5,000
B	0.2	2,000
C	0.1	1,000
D	0.08	800
E	0.05	500

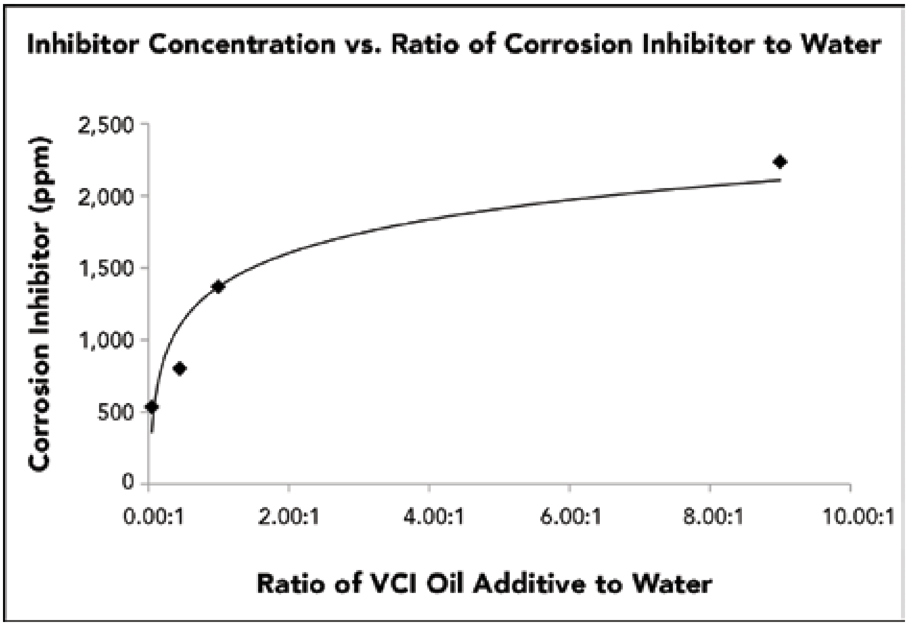

FIGURE 1 Corrosion inhibitor concentration compared to the ratio of VCI oil additive to water from extraction testing.

Al_2O_3 abrasive paper. Panels were cleaned with methanol, weighed to the nearest 0.1 mg, and placed into the respective solutions. Test cells were placed into a 40 ± 2 °C oven for approximately three weeks. At this time, panels were rinsed with methanol, wiped clean with a lint-free wipe, and placed in a cleaning solution as specified in ASTM G01, designation C.3.5 (500 mL HCl, 3.5 g hexamethylene tetramine, and reagent water to make 1,000 mL solution). Panels were then dipped into a solution of commercial corrosion inhibitor at 1% in DI water and dried with a lint-free wipe to prevent further flash corrosion prior to examination of mass loss. The panels were examined for mass loss and the rate of corrosion was calculated as noted in Equation (1).

Three panels were prepared for each tested solution, along with three panels to be tested in DI water as a control. A single prepared, but untested, steel panel was prepared and subjected to the cleaning procedure. The mass loss of the cleaning procedure was determined, and this mass loss was subtracted from the mass loss measured in each tested panel, in order to determine the true mass loss from the immersion corrosion testing.

Electrochemical Corrosion Testing

EIS was performed on several solutions with different concentrations of the corrosion inhibitor identified above in DI water with 300 ppm sodium chloride (NaCl). EIS testing was performed with 10 mV amplitude around open circuit potential (OCP) over a frequency range of 0.01 to 100,000 Hz on a C1018 steel plug and modeled using the Randles equivalent circuit. The inhibitor efficiency was calculated by comparing the polarization resistance (R_p) of the control against the experimental polarization resistance (Equation [3]).

$$\textit{Inhibitor Efficiency} = \left(1 - \frac{\textit{Control } R_p}{\textit{Experimental } R_p}\right) \times 100\% \qquad (3)$$

Extraction of Corrosion Inhibitor from VCI Oil Additive

Extracted solvent samples were submitted for analysis of organic nitrogen content according to the Kjeldahl Method. Results were received in ppm of organic nitrogen in the sample. The amount of corrosion inhibitor (in ppm) was calculated based on the ratio of nitrogen in the corrosion inhibitor molecule (Table 2).

As the ratio of VCI additive to water increased, the concentration of corrosion inhibitor increased in kind. As shown in Figure 1, the inhibitor partitioning seemed to plateau at high VCI additive ratios. Based on the results, a wide range of corrosion inhibitor concentrations were evaluated in immersion testing to observe the effect of varying concentrations on inhibitor on the corrosion protection efficiency.

TABLE 4 Immersion Testing Results—First Iteration

Sample	Inhibitor (ppm)	Starting Mass (g)	Ending Mass (g)	Mass Loss (mg)	Corrosion Rate (mpy)	Corrosion Reduction (%)
Control	—	31.923	31.835	87	1,432.7	—
A	5,000	31.476	31.476	0	0.0	100
B	2,000	32.140	32.139	1	16.5	99
C	1,000	31.558	31.537	21	345.8	76
D	800	32.461	32.410	51	839.9	41
E	500	32.159	32.140	20	329.4	77

TABLE 5 Immersion Testing Results—Second Iteration

Sample	Sample No.	Inhibitor (ppm)	Starting Mass (g)	Ending Mass (g)	Mass Loss(A) (mg)	Corrosion Rate (mpy)
Control	1	—	32.298	32.207	89	1,613.9
	2		32.394	32.313	78	1,414.4
	3		32.316	32.246	68	1,233.1
A	1	5,000	32.235	32.233	0	—
	2		32.090	32.087	0	—
	3		32.378	32.376	0	—
B	1	2,000	32.272	32.270	0	—
	2		32.173	32.171	0	—
	3		32.108	32.105	0	—
C	1	1,000	32.014	32.012	0	—
	2		31.889	31.887	0	—
	3		31.969	31.967	0	—
D	1	800	32.125	32.123	0	—
	2		32.319	32.317	0	—
	3		32.144	32.142	0	—
E	1	500	32.094	32.084	7	126.9
	2		32.153	32.150	0	—
	3		32.280	32.278	0	—

(A)Calculation includes the correction for mass lost during the panel cleaning procedure.

It is noted in Table 2 that Sample No. 1 and Sample No. 4 are the most representative for recommended applications. The control sample analyzed was found to have no organic nitrogen content, as expected.

Immersion Corrosion Testing

Based on the results of the extraction testing, the following concentrations were selected to evaluate the effectiveness of the partitioned corrosion inhibitor in solution. Samples were prepared as described in Table 2 and labeled as shown in Table 3.

First Iteration of Test

Immersion testing was conducted for 479 h to assess the level of corrosion protection provided at various concentrations. As shown in Table 4, increasing inhibitor concentration in general showed improved corrosion protection. Corrosion rate reduction was above 75% for most samples. While it would be expected to see the corrosion rate in Sample E be higher than that of Sample D, this was not the case in the first iteration of immersion corrosion testing.

Note that the mass loss from the panel cleaning procedure was determined to be negligible. Mass loss values represent the mass loss values measured during testing.

To better explore the results, the second iteration of immersion corrosion testing was performed.

Second Iteration of Test

The second iteration of immersion corrosion testing was conducted for 435 h. As shown in Table 5, more careful sample preparation and cleaning, as well as eval-

TABLE 6 EIS Testing Results

Inhibitor (ppm)	OCP (mV)	R_p (kΩ)	Inhibitor Efficiency (%)
0	–451.0	0.794	0.0
100	–428.0	1.396	43.1
500	–379.4	12.25	93.5
2,000	–376.7	25.64	96.9
5,000	–231.8	43.24	98.2

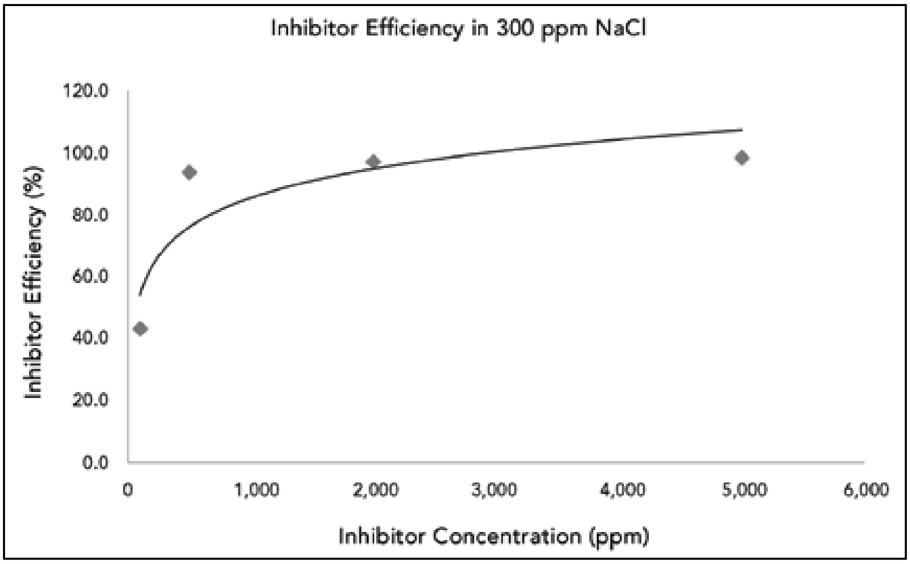

FIGURE 2 Inhibitor efficiency compared to the concentration of corrosion inhibitor from EIS testing.

uation of samples in triplicate provided much more consistent results. The presence of corrosion inhibitor at the lowest concentrations of 500 ppm showed a significant effect on the corrosion rate, eliminating corrosion on all but one sample.

The mass loss of the cleaning procedure was determined to be ~3 mg. The mass loss is the measured mass loss after testing, minus this 3-mg value. Due to rounding, some mass loss values after this correction would be listed as "–1 mg," typically indicating a mass gain. These values are reported as 0 mg in Table 5.

Inhibitor concentrations of 800 ppm or greater provided excellent corrosion protection, resulting in a corrosion rate of 0 mpy, corresponding to a corrosion rate reduction of 100%. One sample with inhibitor concentration of 500 ppm did show some corrosion over the course of testing, corresponding to a corrosion rate of 126.9 mpy, or a corrosion rate reduction of 91.1% (calculated with Equation [2] using the average corrosion rate of control Samples No. 1, 2, and 3).

Electrochemical Corrosion Testing

EIS testing was performed on the corrosion inhibitor of interest at various concentrations. The test solution utilized a 300-ppm concentration of NaCl in DI water to increase the conductivity and corrosivity of the system. The results of this testing show a marked increase in the polarization resistance to 1.396 kΩ with just the addition of 100 ppm inhibitor and an even higher resistance when the inhibitor is dosed according to the concentrations tested above. This data is represented in Table 6 and Figure 2.

Conclusions

Extraction testing, based on the manufacturer's various recommended applications of the VCI oil additive, shows that corrosion inhibitor partitioning results in a concentration of roughly 800 to 1,350 ppm in the aqueous phase, depending on the application method of the VCI oil additive. These results provide a benchmark for corrosion testing, to test the partitioned corrosion inhibitor for its protection capabilities in a controlled setting.

Initial immersion corrosion testing provided promising results, showing >75% corrosion rate reduction at even the lowest concentration of inhibitor. When reevaluation was performed in triplicate, even better results were seen, showing a complete reduction in corrosion rate in all but one case.

It is likely that initial factors such as cleanliness of metal surfaces or the presence of other materials or contaminates can influence the corrosion rate. In the context of the real-world application being evaluated, metal surfaces may not be completely clean, and contaminates may be carried into the system by the water as it ingresses. While all these factors may affect the corrosion protection provided by the corrosion inhibitor that partitions from the oil phase to the intruding aqueous phase, it is shown that corrosion inhibitor that naturally partitions into the aqueous phase from the treated oil phase may provide corrosion protection in that system.

Results from EIS reinforced the results obtained via immersion testing. Concentrations of inhibitor that were much lower than what would be expected in a layup scenario returned polarization resistance values that were notably higher than the non-treated solution. It should also be noted that the chloride concentration utilized in the EIS testing performed would only be seen in very contaminated systems in actual application. The significant levels of corrosion inhibition observed in such a contaminated system effectively demonstrate the potential protection that can be realized by the passive partitioning of inhibitor from the oil phase into the aqueous phase.

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