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SUPPLEMENT TO **JUNE 2015**

MP MATERIALS PERFORMANCE

CORROSION PREVENTION AND CONTROL WORLDWIDE

PRESERVING INDUSTRIAL STRUCTURES AND EQUIPMENT

Comparing Vapor Corrosion Inhibitors with Dry Air Systems

Packaging Materials Made from Barrier-Coated Paper

Improving Waterborne Acrylic Coatings

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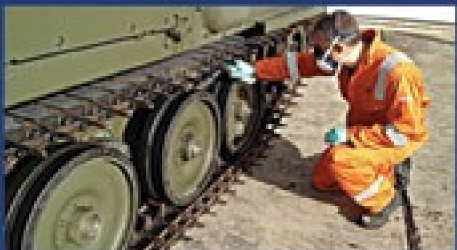

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MP

CORROSION PREVENTION AND CONTROL WORLDWIDE

MATERIALS PERFORMANCE

About the Cover

Corrosion protection of pressure vessels, turbines, and other industrial structures, equipment, and operational spare parts is an ongoing issue worldwide. Many factors must be considered when determining best practices for asset preservation, including length of protection, accessibility, type of equipment, and environmental and storage conditions. The article beginning on p. 6 explores the use of volatile corrosion inhibitors in both laboratory and real world settings compared to other corrosion control systems, and costs of each are compared.

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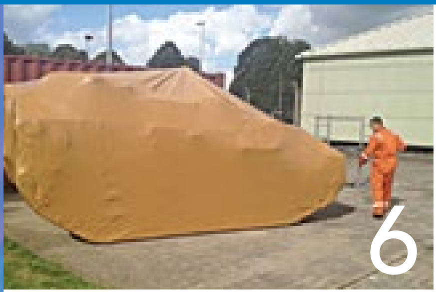

TABLE OF CONTENTS

PRESERVING INDUSTRIAL EQUIPMENT

INHIBITOR TESTING

RECYCLABLE PROTECTIVE PACKAGING

IMPROVING WATERBORNE ACRYLIC COATINGS

EDITORIAL

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6

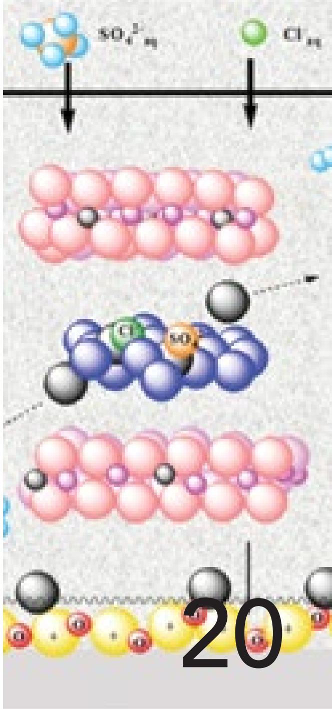
Protecting Assets with Cost-Effective, Environmentally Friendly Technologies

Corrosion control technologies have long been recognized as critical to preserving the world's infrastructure, thereby protecting people, assets, and the environment and minimizing costly repair and replacement work. As much of the world's aging infrastructure reaches the end of its design life, corrosion prevention methods are regularly being developed and improved to ensure reliable performance of everything from tanks, vehicles, and plant equipment to bridges and other structures.

Vapor-phase corrosion inhibitors (VCIs) are examples of an economical class of products that have been refined over the years to offer high versatility and cost-effective performance while maintaining a low impact on the environment. The performance of these inhibitors is driven by the ability to alter the environment where corrosion occurs. They can be designed to form protective barriers on internal or external surfaces or alter the corrosion properties of an enclosed vapor space.

This special supplement to Materials Performance describes several projects and studies involving VCIs, including comparisons with more traditional methods of preserving industrial equipment. Other articles describe packaging materials incorporating VCIs and how they work to protect metal parts during storage and transportation, and water-based acrylic coatings that are made more effective by incorporating nanoparticle VCIs.


10



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Salt Fog	ASTM B117 ASTM B368 (CASS)	Coatings, Lubricants
Vapor Inhibiting Ability (VIA)	MIL-STD-3010B CC-027	Crystalline, Liquids, VCI Coated Materials, VCI Containing Films
Immersion Corrosion Testing	ASTM G31 CC-026	Additives, Corrosion Inhibitors for Water
Electrochemical Polarization Measurements	ASTM G5 C-030	Water Based Electrolytes
Electrochemical Impedance Measurements	ASTM G106 CC-022	Concrete Samples with Rebars
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Evaluating Efficacy of Volatile Corrosion Inhibitors vs. Traditional Methods for Preservation of Industrial Equipment and Operational Spare Parts

Eric Uutala, Cliff Cracauer, and Boris A. Miksic, FNACE, *Cortec Corp. , St. Paul, Minnesota*

Corrosion protection of industrial equipment and spare parts during mothballing and deep storage is an ongoing issue worldwide. Many factors must be considered when determining best practice for asset preservation. Length of time, type of equipment, accessibility, preventative maintenance schedule, and environmental and storage conditions have the greatest influence, while other conditions may also need to be considered. Traditional preservation methods such as nitrogen blanketing, desiccation, or heavy, wax-based surface-applied coatings can be costly to implement and maintain, and can become even more costly if they fail. Incorporation of volatile corrosion inhibitor (VCI) systems is an effective method to replace traditional preservation programs. These systems are often more cost effective to implement, have little to no maintenance cost, and have less failures in long-term preservation programs. In this article, VCI systems are explored in both laboratory and real world settings, compared to traditional systems and costs of each are compared.

Extensive research has been done on the topic of mothballing and layup procedures using volatile corrosion inhibitors (VCIs).[1] Effective preservation of industrial equipment and operational spare parts requires many considerations. These considerations follow.

Length of Protection

Short preservation times can mean high protection costs. Often, this leads to an approach where no VCI or other traditional methods of protection are used, because the upfront cost of preservation is perceived to be too high.

Conversely, long-term protection leads to low cost of protection. In this case, while clients will see the value in preservation, they struggle to determine the best method. Decisions are not always made based on the technical validity of the method, but rather convenience of application and/or inspection. Examples would include the use of humidity indicator cards or coupons to determine the presence or absence of corrosion protection within a package.

Accessibility

Storage in remote areas (jungle, undeveloped locations) creates challenges in corrosion monitoring and replenishing protection. Equipment design can create further challenges related to accessing some of the internal spaces and other critical areas that require protection.

Type of Equipment and Replacement Value

Value of equipment can be critical. However, the more important factor is replacement lead time and/or amount of time to rework equipment that is corroded. Unique or specially designed equipment often have long lead times if a replacement is required. This can lead to downtime at a plant, which can be orders of magnitude more costly than the equipment itself. Therefore, the cost of protection and preservation is irrelevant compared to the value of protecting the asset and the work time it provides.

Steam turbines, for example, are subject to regular, short-term down time for maintenance. In this time, corrosion can occur on ASTM A470[2] steel blades and discs. Specifically, these surfaces are subject to stress corrosion cracking (SCC), crevice corrosion, and hydrogen embrittlement. VCI liquids have been tested as effective corrosion preventives in this application.[3]

Preventive Maintenance Schedule

Equipment and spare parts may have a regular preventive maintenance schedule, with weekly, monthly, or yearly inspections. Or, they have no scheduled inspection after the preservation process. This can have a significant impact on the preservation system used on a specific piece of equipment.

Environmental and Storage Conditions

Arguably, this is the most important factor to consider in any preservation job. Material selection will vary greatly depending on the conditions in which the equipment will be stored, ranging from tropical coastal conditions to climate-controlled warehouses.

Costs of VCI Protection Methods vs. Traditional Layup Methods

The total cost of preservation can be determined based on the specific method chosen. When using a method such as a nitrogen blanket, the cost of the nitrogen generator must also be considered. With a heavy-duty wax-based coating, removal time must be considered. Table 1 outlines the basic costs involved with traditional layup methods, compared to similar VCI systems.

The same costs would apply to protecting the internals of a piece of equipment, such as a pressure vessel (Table 2). However, a secondary VCI liquid can be used specifically for void space protection.

Material costs were calculated based on product cost combined with recommended application/dosage rate. Utilizing a VCI system of liquid and shrink film (250 µm), this piece of equipment can be preserved for $1,000, which includes the cost of material and all equipment needed.

When considering the cost of a system, setup and removal cost must also be considered. VCI products can be flushed or sprayed with water, in the case of VCI liquids, or simply removed, in the case of VCI shrink film. Traditional methods may require harmful solvents and/or time-consuming procedures for removal and disposal. Nitrogen blanketing often requires hours of monitored leak testing prior to final purge.

Experimental Procedure

The efficacy of VCI technology for corrosion protection of industrial equipment and spare parts during layup has been confirmed via multiple laboratory test methods, as well as real life applications (Figure 1).

TABLE 1. COST COMPARISON OF PRESERVATION METHODS ON 20 BY 20 BY 10 FT (6.1 BY 6.1 BY 3.05 M) PIECE OF EQUIPMENT (EXTERNAL)

Product	Material Cost	Equipment Cost	Total Cost
Wax-based coating	\$120[4]	\$150 to \$950[5-6]	\$270 to \$1,070
VCI Liquid A	\$5	\$150 to \$950	\$155 to \$955
MIL-PRF-131[7] barrier film	\$0.18/ft^2 (0.017/m^2)[8]	\$5,000 to \$6,500[9-11]	\$5,180 to \$6,680
VCI shrink film (250 µm)	\$0.08/ft^2 (\$0.0074 m^2)	\$650[12]	\$730
Nitrogen blanket	N/A	\$5,000 to \$20,000+	\$5,000 to \$20,000+
Desiccant	\$0.31/ft^3 (\$0.0088 m^3)	None	\$1,240

TABLE 2. COST COMPARISON OF PRESERVATION METHODS ON 20 BY 20 BY 10 FT VESSEL (INTERNAL)

Product	Material Cost	Equipment Cost	Total Cost
Wax-based coating	\$120	\$150 to \$950	\$270 to \$1,070
VCI Liquid B (internal)	\$540	\$150 to \$950	\$690 to \$1,090
Nitrogen blanket	N/A	\$5,000 to \$20,000+	\$5,000 to \$20,000+
Desiccant	\$0.31/ft^3 (\$0.0088 m^3)	None	\$1,240

FIGURE 1 Fully preserved military equipment using an integrated VCI system.

FIGURE 2 VIA test setup with VCI film.

Laboratory Testing—Vapor-Inhibiting Ability (VIA) Method

NACE TM0208-2008[13] was designed to determine the vapor-inhibiting ability of VCI products. In this test, carbon steel plugs are polished with sandpaper, cleaned with methanol, and then placed within a jar apparatus. VCI packaging is hung from the underside of the jar, ensuring that the VCI does not contact the steel plugs (Figure 2). The jar is sealed and allowed to sit in ambient laboratory conditions for 20 h. At this point, a glycerin and water solution is introduced, and humidity is created. The jars are allowed to sit for 2 h and are then placed in an oven set at 40 ± 3 °C for 2 h. The jars are then opened, and the steel plugs are visually inspected (Figures 3 and 4).

The NACE test method was modified as follows: first, steel plugs were cleaned with an ambient temperature methanol dip, as opposed to a 60-s boiling methanol immersion. Further, the plugs were hand dried with a lint-free wipe, as opposed to a heat gun or hair drier, per TM0208.

This type of test is especially relevant for VCI materials that will be used in mothballing and layup applications, since many of them will never be in direct contact with the metal surfaces they are meant to protect. If the products are unable to pass this test, they will likely fail in preservation applications as well. VCI shrink films are regularly run to a modified version of NACE TM0208-2008 to ensure their efficacy.

Laboratory Testing—VCI Packaging vs. Barrier Film for 15-Year Storage

In preparation for a 15-year build ahead storage program, automotive transmission components were wrapped in one of the fol-

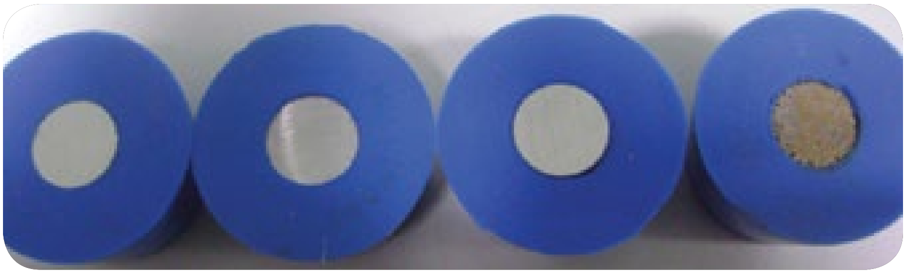

FIGURE 3 VIA test results with VCI shrink film. Control plug is on the far right.

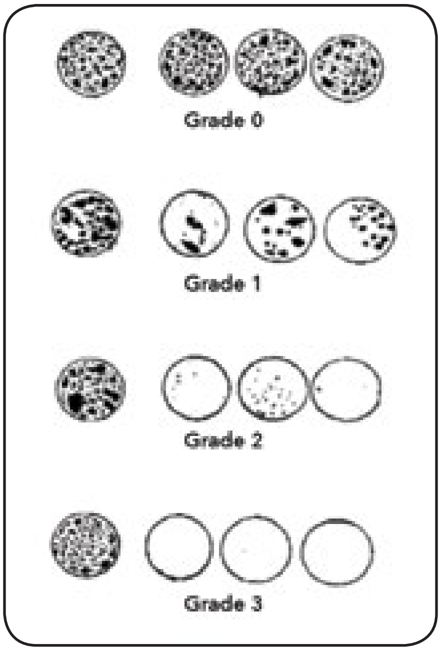

FIGURE 4 VIA test grades.

FIGURE 5 Automotive transmission component after 16 weeks in modified ASTM D1748 testing, wrapped in VCI film.

FIGURE 6 VCI aerosol used to protect combat vehicle reconnaissance (CVR) wheels. VCI additives were also used in the fuel, coolant, engine, gearbox, drive, and brake systems.

FIGURE 7 CVR wrapped in VCI shrink film, in place for final preservation.

lowing: a single-layer VCI film, a multi-layer VCI film, or a standard foil barrier film. After being wrapped, components were exposed to modified ASTM D1748[14] conditions. Test conditions were 49 °C (120 °F) and constant condensing humidity, per ASTM D1748. However, the test was much larger than that of the standard, in order to allow the number and size of components to be tested. As such, the wrapped components were not in constant rotation, per the standard. Parts were removed, unwrapped, visually inspected, and photographed on a four-week schedule, for a total of 20 weeks (Figure 5).

Real World Analysis

VCI preservation systems have been used in military and industrial applications worldwide for over 60 years. More recently, these projects have focused on vehicle and heavy equipment preservation, which addresses multiple systems, starting with grease points along the axle, moving to all relevant fluid reservoirs (oil, fuel, coolant, etc.), and finishing with a VCI shrink wrap around the entire piece. The goal is to leave a vehicle or piece of equipment that is completely preserved, but ultimately ready for use at a moment's notice.

Results and Discussion

VIA Test

VCI films (both shrink and standard) are regularly run through VIA testing to ensure that they can provide effective corrosion protection while not in contact with the metal surface. Figure 2 shows the test setup. Figure 3 represents typical VIA results for an effective VCI film.

Laboratory Testing—VCI Packaging vs. Barrier Film for 15-Year Storage

After 20 weeks of modified ASTM D1748 testing, the most effective corrosion protection system was with a multi-layer VCI packaging system.[15] This system was implemented for the 15-year warehouse storage program, and no corrosion claims were made during that time.

Real World Analysis

VCI preservation systems have been successfully used around the world in military and heavy industrial applications, on vehicles, various pieces of equipment, and critical operational spare parts. Storage conditions have ranged from indoors (temperature-controlled warehouses) to outdoor, tropical conditions. Applications have been successful in all of these areas. Figures 6 through 13 show examples of VCI preservation systems being used on a variety of equipment.

Conclusions

For more than 60 years, VCIs have been effectively implemented into preservation applications worldwide. VCI films are an integral part of these systems, and they will provide protection both in contact and vapor phase, as shown in NACE TM0208-2008. Multi-layer VCI packaging systems have been successfully implemented in preservation of operational parts for programs lasting over 10 years, with no corrosion claims.

In the case of larger pieces of equipment, more diverse VCI systems have been effectively implemented for preservation. These types of systems have been used for the United States Armed Forces and the United Kingdom Ministry of Defense,[16] along with many manufacturers of heavy industrial equipment.

Additionally, VCI systems provide a preservation method that is cost neutral at worst, and in many cases provide a cost benefit compared to traditional chemical methods. This does not take into account the labor savings, performance capability, or disposal costs, which can be difficult to quantify when speaking in generalities. When compared to nitrogen or dehumidification systems, VCI preservation programs provide a clear cost and performance benefit. Additionally, they can be implemented in virtually any environment, as they do not require access to power or other utilities needed to provide continuous protection and monitoring over an extended period of time. VCIs provide an effective layup and mothballing system that traditional methods cannot meet from a cost or performance standpoint. Equipment costs are minimal for application, as are costs associated with maintenance, cleanup, and disposal of waste materials.

FIGURE 8 United States Air Force cargo loader, preserved with VCI shrink film.

FIGURE 9 Three United States Air Force cargo loaders, preserved with VCI shrink film.

FIGURE 10 Gas turbine shells, prior to preservation.

FIGURE 11 Gas turbine shells, after preservation with VCI shrink film.

FIGURE 12 Rotor being cleaned prior to preservation.

FIGURE 13 VCI shrink film being applied to rotor.

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BORIS A. MIKSIC, FNACE, is president and chief executive of Cortec Corp. He has served in this capacity for 38 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

Comparison of the Corrosion Protection Effectiveness of Vapor Corrosion Inhibitors and Dry Air System

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

The corrosion behavior of carbon and galvanized steel samples was investigated in two test environments containing 200 ppm chloride solution. The first set up used 10% inhibitor, while the second used dry air to maintain moisture levels below 40% relative humidity at 20 psi (0.14 MPa) applied pressure. The corrosion rates of the exposed samples were monitored for more than six months (roughly 4,464 h) using electrical resistance (ER) probe techniques. The data demonstrated that the inhibitor provided superior corrosion protection for the steel samples. The samples in the dry air system suffered corrosion attack and red rust formation after 21 days. The ER probes showed a corrosion rate of less than 0.08 mpy with inhibitor, while the dry air samples showed, worst case, a 1.6 mpy (2.03 µm/y) corrosion rate and ER probes were heavily corroded..

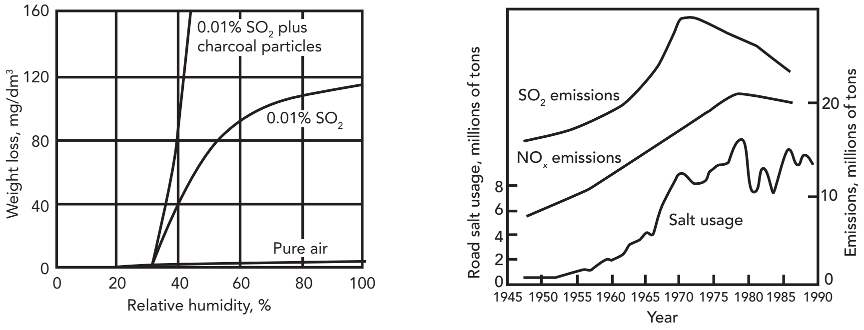
Over the past 20 years, various corrosion protection systems have been implemented to improve structural longevity. These implementations have been worldwide, as corrosion concerns affect all industrialized countries, including Japan (with the Innoshima, Ohnaruto, and Akashi-Kaikyo Bridges),[1] Denmark (the Danish Faroe, Great Belt, and Little Belt Bridges), Sweden (Högakusten Bridge),[1-2] South Wales (Severn Bridge),[3] France (Aquitane Bridge), China (Rung Yang Bridge), and the Middle East (Qatar Lusail Bridges).[2] In the United States, there are numerous complications regarding infrastructure, military equipment and aging aircraft due to atmospheric corrosion.

On several of the bridges in Japan, high-strength cables (typically steel that has been hot dip galvanized in zinc) were suffering from advanced states of corrosion (cracking and swelling) due to inadequate paint coatings and high levels of humidity.1 The common element in all of the "fixes" or improvements made to subsequent bridge construction was the addition of dry air; that is, the use of a dehumidification system. This was either a retrofit or part of the new construction. Two countries, Norway (Hálogaland and Hardanger Bridges) and Japan, have required dehumidification systems in all bridge construction since 2009.2

It has been estimated that between $2 trillion and $4 trillion are lost to corrosion each decade.[4] In atmospheric corrosion, a material is subjected to air moisture and corrosive species (pollutants).[5] Corrosion, the natural degradation of materials due to interactions with the environment, can be uniform or localized. The vast majority of natural degradation, however, is uniform, and atmospheric corrosion is probably the most prevalent type.[6] Atmospheric corrosion is generally a serious risk to metals that are exposed to the environment. The U.S. Government reports that corrosion damage for military defense exceeds $20 billion per year.[7] Preservation and mothballing equipment during short-term or long-term storage is extremely important to maintain access and military preparedness.

Common techniques used to reduce humidity or isolate the metal from moisture, including physical barriers such as paints and lubricants, will lessen the corrosion rate significantly. Concern for the environment and desire to minimize use of hazardous chemicals has led to system modernization and the development of new technologies for barrier coatings. An alternative approach, controlled humidity protection, focuses on the air moisture, specifically relative humidity (RH). Elimination of moisture is critical for suppressing the corrosion rate in atmospheric corrosion. By extracting moisture from the air, RH can be reduced to a level where surface wetness cannot form.[8] The processed dry air is then recirculated around the equipment. Dehumidification is effective—it has been determined that steel is much less likely to corrode in environments with less than 40% humidity.[2,5] Reducing the temperature does not always help and reducing the pollutant concentration is not always achievable.

Controlled humidity protection (CHP) has been extensively evaluated and is applied by many nations as a maintenance technology for operational weapon systems. Within the Department of Defense



(a) (b)

FIGURE 1. Custom ER probe for casings.

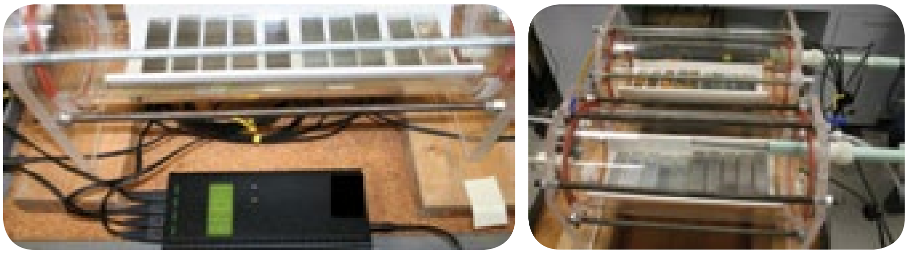


FIGURE 2. Test setup for the controlled humidity corrosion tests on UNS G102000 steel and galvanized steel samples. ER probes were in environments with 10% VCI or nitrogen blanketing at 10 psi applied pressure.

(DoD), the Army National Guard is a proponent of applying CHP to its weapon systems. Independent studies and analyses performed by the DoD Inspector General and Army Cost and Economic Analysis Center validated the significant benefits achieved with controlled humidity protection.[8] Many foreign defense forces currently use CHP as a maintenance technology for their operational weapon systems.

An industry analysis of 11 European defense forces[2,9] revealed that the majority have instituted CHP technology in both operational and longer-term applications. The tangible benefits of CHP as a maintenance technology can include reduced ownership costs for weapon systems and equipment, and increased readiness and sustainability.[8] Despite positive data, localized corrosion attacks have been reported for this method of corrosion protection. When a system is breached and pollutants or contamination enter the dry air system, localized corrosion can occur.

Atmospheric corrosion is an electrochemical process initiated by a thin layer of moisture on the metal surface. The composition of the electrolyte depends on the deposition rates of the air pollutants and varies with the wetting conditions.[10] Corrosion severity is affected by humidity, pollutants, and temperature.[6] Humidity is a necessary component for corrosion to occur, but it is not the only factor. Even in very humid environments, corrosion of uncontaminated surfaces is often relatively low.

Pollutants or other atmospheric contaminants increase atmospheric corrosion by enhancing the electrolytic properties and stability of water films that condense from the atmosphere. Sulfur dioxide (SO_2), carbon dioxide (CO_2), nitrogen dioxide (NO_2), Cl-, and F- are common industrial pollutants. The corrosion rate will increase if the pollutants react with the surface water to create a low pH environment (acidification) and compromise the protective oxide film on the metal surface.[5] Other causes are formation of hygroscopic films (water absorption without formation of bonds) as a result of corrosive byproducts and precipitation of salt particles. They reduce the relative humidity necessary to cause water condensation and enhance the presence of a water film that increases the time of wetness and the consequent extent of corrosion. Only when the relative humidity is below a critical value for existing contaminants, will the film formation be suppressed and corrosion minimized.

In Figure 1(a), the effect of 0.01% SO_2 on the corrosion rate (weight loss of steel) as compared to pure air can be seen. RH seems to be less significant than the air quality. Despite 100% RH, the graph shows no increase in weight loss (rusting of iron) if pollutants are not present.[10] Figure 1(b) shows road salt usage for the United States in millions of tons, the point being there is no shortage of atmospheric pollutants to exacerbate corrosion.

Vapor phase corrosion inhibitors (VCIs) are an alternative protection method that is both effective at controlling corrosion and inexpensive. A VCI is a volatile compound and must form a stable bond at the interface of the metal, preventing penetration of corrosive species.[11-16] VCIs offer an alternative way to protect stored equipment, facilities, and their contents. These inhibitors are easy to apply, versatile, and can be used to protect multiple metal types in a variety of industries. These materials have stable passivating properties, strong tendencies toward surface adsorption, and the ability to form a comparatively strong and stable bond with the metal surface.[17-18] Compared to other methods of corrosion prevention such as inert gas blanketing and dehumidification, VCIs provide substantially better corrosion control at lower cost and require a very low dosage rate. Controlled humidity protection in combination with VCI injection has recently been used to control the corrosion in main cables on suspension bridges, where traditional methods have been unable to adequately protect them.[3]

The inhibitors are water-based and ideal for equipment with complex geometries such as boilers, heat recovery steam generators, and pressure vessels, for mothballing, and short-term storage applications. This method can also minimize corrosion attack where there are restricted geometries, notches, crevices, underdeposits, and laps. VCI forms a solution in water and when applied by spraying or dipping, will protect ferrous and nonferrous

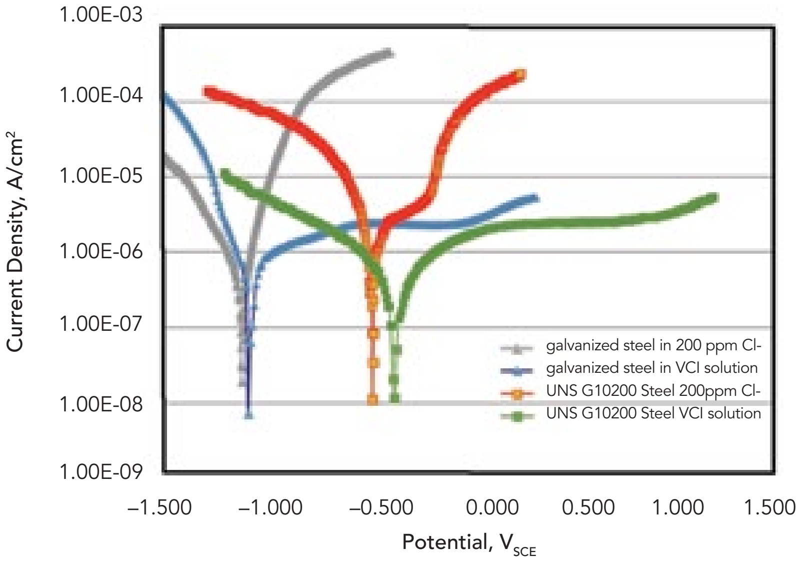


FIGURE 3. Electrochemical polarization behavior of the UNS G10200 steel samples in 10% VCI and dry air in 200 ppm chloride ion solution.

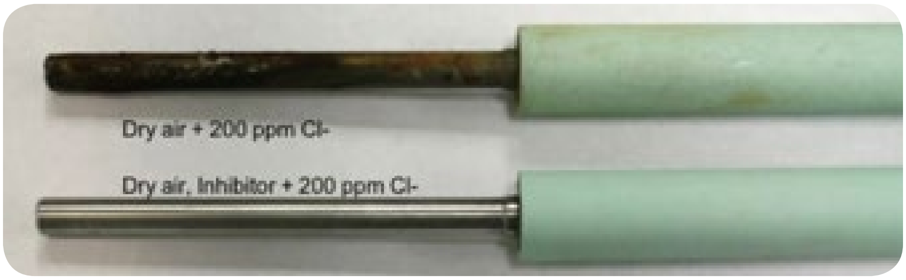


FIGURE 4. ER probes after 4,464 h exposure; top probe exposed to dry air, lower probe protected with inhibitor.

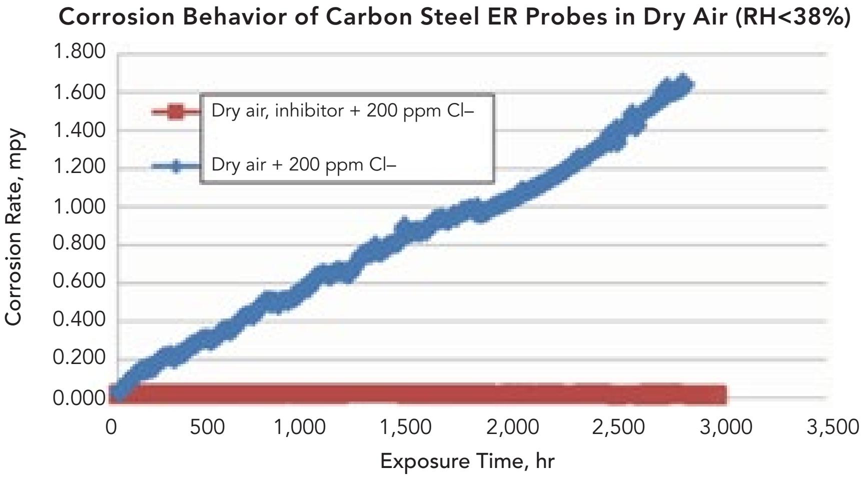


FIGURE 5. Comparison of corrosion on steel probes in VCI and dry air protection system. There is a much lower corrosion rate for steel samples protected by VCI (average corrosion rate of 0.04 to 0.08 mpy), while dry air system resulted in increasing attack with corrosion rate as high as 1.6 mpy.

metals, including castings, tubular parts, finished parts, gears, pumps, housings, structural steel, sintered metals, bars, and roll stock. VCI has excellent wetting properties and forms a clear, dry, hydrophobic film of roughly 0.25 mils (6.35 µm) thick on the surface that is stable up to 350 °F (176 °C).[11]

Adsorption of the inhibitor onto the metal surface provides a protective inhibitor layer. As well, the vapor phase action protects surfaces that have not been directly coated and are difficult to reach. This type of corrosion inhibitor is useful when oil, grease, or other adherent films are not practical. The inhibitor is transmitted by vapor that is controlled by the crystal lattice structure and atomic bond characteristics of the molecule.[14-15] The protective vapor expands within the enclosed space until the equilibrium determined by its partial pressure is reached; the higher the vapor pressure, the sooner the saturation of protected space. The VCI organic chemistry is free of hazardous amines, nitrites, and phosphate ester. There are no hazardous decomposition byproducts. Furthermore, the product is biodegradable and non-flammable unlike some of the earlier chemicals tested in the 1940s and 1950s like dicyclohexyl ammonium nitrite, ammonium nitrite, urea, and acetamide.[19]

The corrosion inhibition mechanism was determined to be the physical adsorption of inhibitor molecules to the metal surfaces.[20-21] Physical adsorption requires energy between -5 to -20 kJ/mol.[13-14] The analysis of the inhibitor showed an enthalpy of adsorption in the range of -14 to -18 kJ/mol.[20-21] Generally, chemisorption requires more energy and results in stronger bonding between the molecules and the surface of the substrate, which forms a more stable protective film.[18] The majority of corrosion damage to turbo-machinery systems, however, occurs during the shutdown period due to chemistry changes and stagnant conditions in localized areas. Therefore, a corrosion inhibitor with strong physical adsorption to the metal surface will provide satisfactory protection and does not require strong chemical bonding.

Experimental Procedure

Corrosion behavior of carbon steel (CS) and galvanized steel samples were studied in two different controlled humidity protection conditions; the first environment contained 200 ppm chloride solution plus 10% inhibitor (VCI), and the second test environment included 200 ppm chloride solution (injected into the environment every 48 h) with a constant flow of dry air at less than 40% RH and 20 psi (0.14 MPa) applied pressure. The corrosion rates of the exposed samples were monitored for more than six months (roughly 4,464 h) using electrical resistance (ER) probe techniques. RH and temperature of each test chamber were monitored by the Sensirion[†] sensors and data logging software. The temperature sensor and the humidity sensor form a single unit. This enables an accurate and precise determination of the dew point, without incurring errors due to temperature gradients between the humidity and the temperature sensors. The sensor elements are integrated with a signal amplifier unit, an analog-to-digital converter, and a calibration data memory, yet the device is only a few square millimeters in size.

Electrochemical polarization standards per ASTM G61[22] and corrosion rate measurements using ER techniques were used to evaluate the behavior of this inhibitor on the steel alloy in 200 ppm chloride solution and to compare with a dry air system. Corrosion data were collected using the Metal Samples MS3500E[†] electrical resistance probe system, a remote data logger capable of measuring and storing data. Further experiments were conducted using Gamry PC4/750 Potentiostat/Galvanostat/ZRA[†] instrumentation and DC105[†] corrosion test software. Samples were polished (600 grit), placed in a flat cell, and tested in deionized water solutions containing 200 ppm Cl- with 10% VCI.

The corrosion test setup for the metal samples is shown in Figure 2. In each case, the ER probes were installed in the chamber. The electrical resistance probe equipment measured the corrosion rate for a UNS G10200 steel probe using 10% VCI and another probe for the dry air system. The corrosion rates for the samples were monitored continuously for roughly 4,464 h (6 months). Samples were visually inspected on a daily basis, and their surface conditions were documented on a monthly basis. Samples were visually inspected and scanning electron microscopy (SEM)/energy dispersive x-ray analysis (EDXA) were conducted using a JEOL JSM-6480LV[†] and Thermo System Seven detector[†].

Results

Cyclic Polarization Behavior

Figure 3 shows the polarization behavior for UNS G10200 steel in 10% VCI with 200 ppm chloride ions. The most noticeable changes are the positive shift in the breakdown potential and expansion of the passive range for these alloys in the VCI. The inhibitor changed the reactivity by reducing the pH level, increased the passivation range significantly, and had beneficial consequences for 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

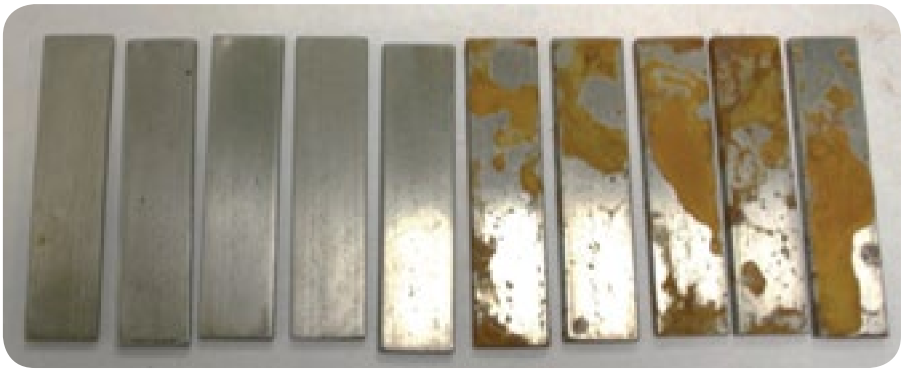


FIGURE 6. Comparison of UNS G10200 steel samples protected with inhibitor (left) and exposed to dry air (right) for 96 days.

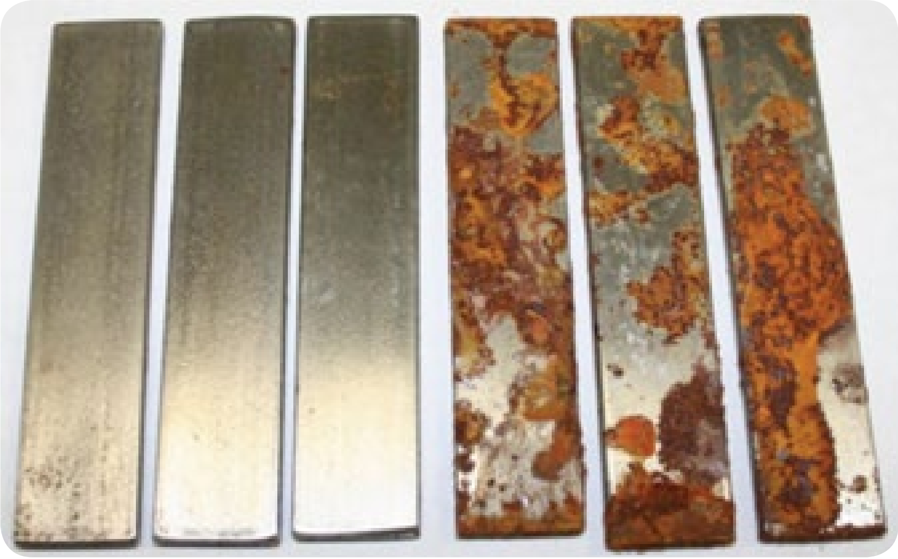
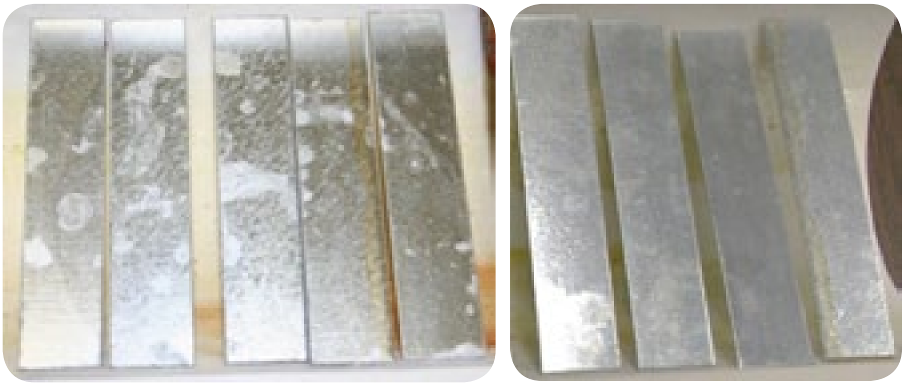


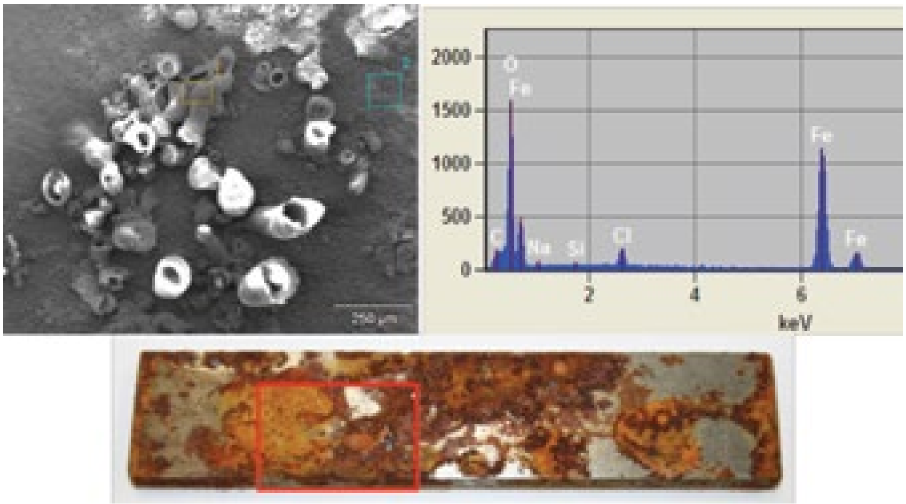
FIGURE 7. Comparison of UNS G10200 steel samples after 155 days: (left) inhibitor still providing protection, (right) samples exposed to dry air in test chamber.



(a) (b)

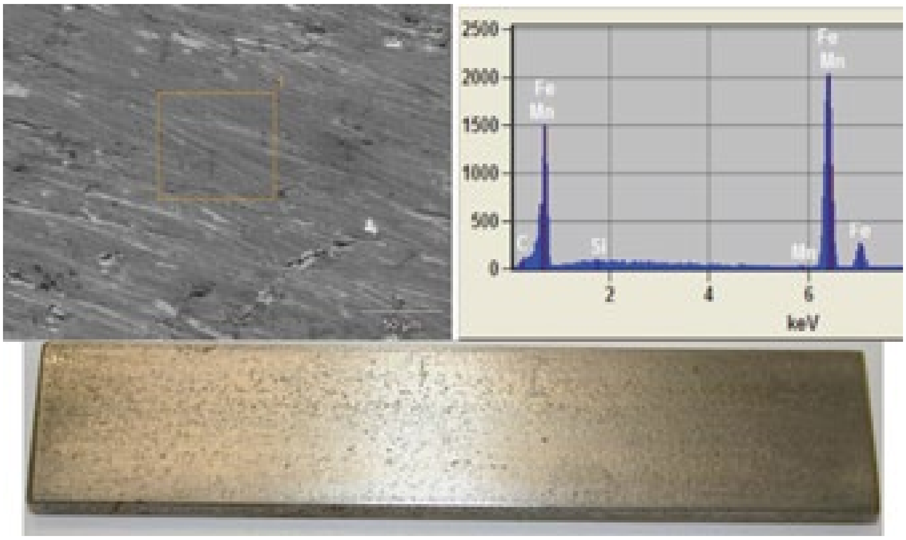
FIGURE 8. Comparison of exposed galvanized steel samples for dry air and VCI test chamber after 155 days; (a) white rust formation is seen on dry air samples, while (b) VCI exposed samples were corrosion-free.

[†] Trade name.



	Weight%				
	C-K	O-K	Na-K	Cl-K	Fe-K
Steel dry air (1)_pt1	5.35	30.01	1.77	0.24	62.63
Steel dry air (1)_pt2	6.04	26.35	1.69	0.43	65.50

FIGURE 9. SEM/EDXA on the steel sample in dry air test chamber after 186 days, showing severe rust formation.



	Weight%			
	C-K	Si-K	Mn-K	Fe-K
Steel dry vci(1)_pt1	4.40	0.40	0.57	94.63

FIGURE 10. SEM/EDXA on the steel sample in dry air plus VCI test chamber after 186 days, showing a corrosion-free surface.

film, and shift of the critical pitting potential to higher levels.

Figure 4 shows the ER probes after 4,464 h exposure in both environments. The ER probe protected by 10% inhibitor (bottom probe) shows no corrosion damage. Corrosion rates for the probes can be seen in Figure 5. The results show that the dry air system is unable to protect the steel against corrosion. Figures 6 through 8 show the progression of corrosion damage to the metal surface over time.

Figures 9 through 11 show the SEM/EDXA results for the steel and galvanized steel samples. The dry air system showed severe corrosion products (chloride rich) while the presence of inhibitor suppressed the formation of corrosion products on the steel surface. Similar results were observed for the galvanized steel sample exposed to dry air only and dry air with inhibitor. The morphology of the corrosion products are identical to atmospheric corrosion of CS and galvanized steel. These observations demonstrate that the addition of inhibitor is critical for protecting the steel structures.

Conclusions

The corrosion test results have demonstrated that corrosion inhibitors have superior advantages over the dry air system. Samples that were exposed to dry air showed corrosion attack and red rust formation after 21 days of exposure. ER probes showed a corrosion rate of 0.04 to 0.08 mpy for VCI-treated samples while the dry air samples showed a 1.3 to 1.6 mpy corrosion rate and ER probes were heavily corroded. The dry air exposed samples showed an increasing trend, indicating inability of controlled humidity protection to retard corrosion once the corrosion reaction had started. Test results showed that a dry air system is not an effective method to retard corrosion.

Electrochemical polarization behavior showed the addition of VCI to the environment expands the region of stability of the passive film. The passive film breakdown potential for VCI-treated steel samples increased by nearly 1.0 V, indicating less susceptibility to localized corrosion.

In summary, the VCIs provide effective corrosion protection for steel materials exposed to the environment for short-term storage. Although controlled humidity protection systems, in theory, can suppress the cathodic reaction and lower the corrosion rate, in reality the amount of moisture and oxygen that is required to initiate the corrosion reaction for steel is still extremely low. A dry air-controlled humidity system can reduce the moisture level, but it won't be enough to prevent corrosion and the steel sample will corrode. Furthermore, once corrosion begins, the dry air system cannot retard the accelerating corrosion reaction. The advantage of the VCI is the creation of a strong physisorption to the steel surface that minimizes any surface contact with corrosive species due to its hydrophobic film. Therefore, VCIs have superior advantages over the dry air or gas blanketing system in the presence of aggressive environments that contain excessive salt, oxygen, and moisture.

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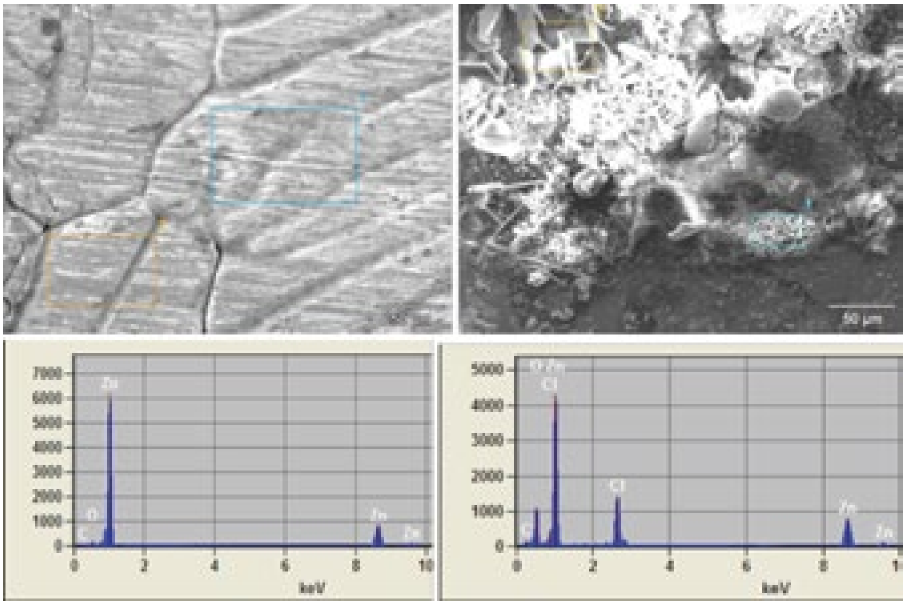

	Weight%			
	C-K	O-K	Cl-K	Zn-K
gal dry(2)_pt1	4.05	20.07	13.61	62.27
gal vci(2)_pt2	10.28	3.12		86.59

FIGURE 11. SEM/EDXA on the galvanized steel samples in dry air with and without VCI addition after 186 days, showing only white rust formation on dry air without VCI addition.

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Improved Packaging Materials Made from Barrier-Coated Paper Incorporating Vapor Phase Corrosion Inhibitors

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Vapor phase corrosion inhibitors (VCIs) are used for safe and cost-effective protection of a wide range of metal articles. Cellulose-based materials (paper and fiberboard) are desirable packaging materials due to cost, material properties, and environmental attributes (bio-based content, recyclability). These materials can be easily impregnated with VCIs to provide corrosion protection (e.g., for storage and transportation of metal parts). However, uses of these materials can be limited by the water affinity of paper/fiberboard, and the highly porous nature that allows rapid depletion of the VCIs and exposure of the metal to corrosive elements in the surrounding atmosphere. The barrier properties of paper products can be greatly improved with wax or polyethylene coating, but such products are no longer suitable for recycling. Emulsion-based coating products have also been used to improve the barrier properties of paper products. Unfortunately, many of these also reduce suitability for recycling. Some require multiple coats to achieve high barrier properties, thus increasing the product cost. This article presents studies with repulpable barrier coatings that are waterborne and applied in a single coating pass. When combined with VCIs, these provide recyclable packaging materials with excellent barrier properties and cost-effective corrosion protection..

Vapor phase corrosion inhibitors (VCIs) are a well-known and highly versatile range of products for the prevention of corrosion. VCIs can be delivered to the target metal in a variety of ways.

One common product is paper sheeting impregnated with VCIs.[1] Unfortunately, the porous and hydrophilic nature of paper can limit the effectiveness of VCIs in protecting the target metal. Historically, polyethylene (PE) and wax coatings have been used to seal porous paper to provide a moisture barrier and/or moisture-vapor barrier. These coatings also limit the migration of the VCI vapor away from the protected item, thus further improving the product effectiveness. While effective and relatively low cost, these coatings can render the paper non-recyclable, thus diminishing the otherwise positive environmental benefits of paper.[1-3] Numerous alternate paper coating products are available to improve the barrier properties of paper. Of these, waterborne emulsion coatings are attractive based on cost, ease of application, and barrier attributes. Unfortunately many of these also have deficiencies, such as inferior barrier properties, loss of recyclability/repulpability, and/or the need for a primer coat before application of the barrier coat (thus increasing cost).[2-5] In this article, we report the development of an improved VCI impregnated paper with a barrier coating. The product is repulpable and recyclable. The coating is applied in a single coating pass. The article further discusses some of the process variables necessary to achieve optimal coating performance.

Experimental Procedure

Materials

The following materials were used in the test:

- Paper: 40 lb/3,000 ft^2 (unit abbreviated as "#") natural Kraft produced by Cascades (East Angus, Quebec Mill). This corresponds to ~65 g/m^2.
- Coatings tested:
  A: Cortec barrier coating
  B: Keim Additech Ultraseal[†] W-954
  C: S-1601-L polyester based barrier coat
  D: S-1805-L barrier coating
  E: Resin blend formulation (based on DSM Neoresins published formula U4-410[†])
  F: 1SR81A
  G: 1SR81B

Samples identified as C, D, F, and G were provided by SNP, Inc., with the numbers corresponding to their product or experimental sample numbers.

All the above coating formulations are proprietary except for E above. The composition of coating E is shown in Table 1.

[†] Trade name.

The formulation is based on a starting formula, but with substitution of several of the indicated components with similar ingredients. The first three ingredients are the primary functional ingredients. These are: NeoCryl† A-1094 (1) and XK-87 (2), and Byk Cera† Aquacer† 498 (3). Formula E was prepared by mixing the listed ingredients until a homogeneous liquid was obtained. All other products were used as received, generally after stirring to make sure solutions/suspensions were uniform and representative.

TABLE 1. FORMULATION OF COATING COMPOSITION E

ID	Additive	Weight %	Function
1	Proprietary acrylic/styrene copolymer emulsion	50	Binder
2	Proprietary acrylic/styrene copolymer emulsion	42.5	Binder
3	Proprietary nonionic wax emulsion	6	Water resistance
4	Proprietary polysiloxane copolymer emulsion (20% in solvent)	0.2	Defoamer
5	Proprietary acrylic copolymer emulsion	0.3	Thickener
6	2, 4, 7, 9-tetramethyl-5-decyne-4, 7-diol (50% in solvent)	1	Leveling agent

Comparative Samples

A polycoated VCI paper product consisted of PE-coated 40# Natural Kraft with 6# of PE extrusion coated on one surface (produced by Plastic Coated Papers, Inc.), which had VCI solution applied to the non-polycoated side. The dried finished product is available as Cor-pak®† VpCI®† polycoated paper. Commercial wax paper was obtained at a local grocery store.

Methods

Lab Coating

Samples were applied to 8.5 by 11 in (216 by 279 mm) sheets of Kraft paper with Meyer rods (number 6 or 12) to achieve approximate targeted coating weight. Coated samples were immediately dried in a forced air oven at 40 °C for 5 min. The coated paper was then trimmed to 7 by 8 in (179 by 203 mm) to remove edges and uncoated regions. These trimmed samples were further dried for 5 min at 110 °C in a forced air oven to obtain a dry weight. The weight of a dried uncoated paper sample was subtracted to estimate dry coat weight.

Pilot Production Coating

For pilot coating, the selected coating was applied by roll transfer, which was metered by use of an air knife. The coating was dried by means of in-line oven sections to a final moisture content of ~ 6%. Line speed was approximately 400 ft/min (122 m/min). The final VCI-containing product was first coated on one side with the barrier coating. The VCI was applied to the alternate side in a second coating pass. The VCI additive is a proprietary formulation containing ~20% active ingredients and 80% water.

Coating Uniformity

The presence of pinholes, uncoated streaks, or other defects in the surface coating was determined by applying corn oil to the coated surface. Approximately one to three drops were applied to the surface. This was spread evenly with a tissue to coat an area approximately 10 cm on a side. The presence of coating holes/defects became visible within about 1 min, as the oil passed through the holes and became visible as dark spots in the paper.

Water Hold Out

Water hold out was screened by applying drops of water to the coating surface.

Water Vapor Transport (WVTR)

WVTR was determined by a modified version of ASTM E96.[6] Disks of the coated paper were clamped in machined aluminum cells. A rubber gasket provided a seal around the edges. The cells were filled with freshly regenerated silica gel. Filled cells were weighed at the start and periodically over a period of time from one to two days. The cells were placed in a chamber at ~73 °F (23 °C) and 50% relative humidity (RH). Due to modification relative to the official method, the absolute results may differ from those run according to the official method. However, results were found to be highly repeatable, and should provide reliable relative values for comparison of the different coating treatments.

As a check, two samples were tested for WVTR at a commercial testing lab (IPS Testing, Appleton Wisconsin) per the official method, and found to be in good agreement with the results as measured by the modified method.

Oil/Grease Resistance

Samples were tested for grease resistance (oil/grease resistance test) with the use of the 3M† test kit per Tappi Method T559.[7] Samples were further tested by placing a drop of corn oil on the surface and watching for any signs of penetration into the paper.

Repulpability

Repulpability was initially assessed with an in-house method. Briefly, an 8.5 by 5.5-in (140-mm) sheet of the coated paper was cut into ~1-in (25-mm) squares. Approximately 200 mL of 170 °F (77 °C) water was placed in a blender and the blender was turned on. The squares were added (through the lid port) while the blender continued to run. An additional ~100 mL of 170 °F water (300 mL of water in total) was added and the blender was allowed to run for a total of 30 s. The resulting slurry was poured into a shallow tray to examine for the extent of fiber liberation, in comparison to an uncoated paper sample. The final material (overall best performance) was tested at the above-mentioned commercial testing lab according to the FBA method for repulpability.[8] This method was designed to test recyclability of fiberboard, but has become the de facto standard method for assessing recyclability of other paper fiber-based substrates.

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†Trade name.

TABLE 2. COATING WEIGHTS AND WVTR RESULTS

Coating ID	Meyer Rod	Coating Solids Fraction	lb/3,000 ft^2 (g/m^2)			WVTR$^{(A)}$ g/(m^2*d)
			Dry Weight Coated	Net Weight Coating	Predicted Coat Weight	
A	12	0.56	51.2 (83.3)	11.6 (18.8)	9.4 (15.4)	13
B	6	0.45	45.6 (74.2)	6.2 (10.0)	3.8 (6.2)	58
B	12	0.45	46.9 (76.4)	7.2 (11.8)	7.6 (12.3)	57
C	6	0.4	46.8 (76.1)	6.8 (11.0)	3.4 (5.5)	57
C	12	0.4	47.1 (76.7)	7.6 (12.3)	6.7 (11.0)	42
D	6	0.53	47.6 (77.5)	8.1 (13.2)	4.5 (7.3)	39
D	12	0.53	48.6 (79.2)	9.2 (15.0)	8.9 (14.5)	29
E	6	0.47	47.6 (77.5)	7.5 (12.2)	4.0 (6.4)	11
E	12	0.47	48.5 (78.9)	8.6 (14.0)	7.9 (12.9)	11
F	12	0.53	47.4 (77.1)	8.1 (13.2)	8.9 (14.5)	26
G	12	0.53	48.4 (78.8)	9.1 (14.9)	8.9 (14.5)	32

$^{(A)}$WVTR measured at 50% RH and 73 °F (23 °C).

VIA Corrosion Inhibition Test

This testing was performed by standard methods as previously described.[1] In brief, sanded carbon steel (CS) plugs are suspended from a modified lid in a quart jar. Strips of the test substrate (1 by 6-in [152-mm]) are hung from the inside of the lid, being sure they do not come in contact with the plug. The lids are screwed on tight and the jars are left to condition for 20 h at ambient temperature. After conditioning, a glycerol/water solution is added to the jars to accelerate corrosion and left to sit at ambient temperature for 2 h, then in a 40 °C oven for 2 h. The plugs are removed and rated on a scale of 0 (heavily corroded) to 3 (no visible corrosion). A grade of 2 or 3 is considered passing.

Razor Blade–Corrosion Inhibition Test

This testing was performed by standard methods as previously described.[1] In brief, CS panels are cleaned in methanol and dried. Two drops of deionized (DI) water are placed on the metal panel and covered with the substrate of interest. After 2 h, the substrate is removed and the panels are inspected. Panels with any sign of corrosion, pitting, or staining are deemed to "fail" the test. A second test is conducted with copper panels. The method is the same except that a 0.005% sodium chloride (NaCl) solution is used instead of water and the test time is extended to 4 h.

Results

Lab-Coated Samples

Based on manufacturer information and previous experience, it was expected that a dry coating weight of 6 to 12# would be sufficient to achieve a uniform (defect-free) surface coating with barrier properties in the desired range. Given the solids content of the materials, Number 6 and Number 12 meyer rods were used to apply the coating solutions as described in the methods section. Samples were tested for WVTR. The results for coating weight and WVTR are shown in Table 2.

The coating weights were approximately as predicted with use of the Number 12 coating rods. Application with the Number 6 rods resulted in coating weights not greatly different from the Number 12 rods. This may be due to the viscosity and flow properties of the coating solutions, which prevented the formation of a thinner coating layer. Based on the above, a Number 12 rod was used for preparation of all subsequent lab coated samples. By observation, Formula A had a higher viscosity than the other formulations. For high barrier coatings [WVTR < 20 g/(m$^2 \cdot$ d)], WVTR differences between samples of less than ± 3 are not considered to be significant (based on observed variation in test results). For samples with higher WVTR values, the variability of results tends to be greater.

On inspection with oil, all samples (used in the WVTR test) showed good coating uniformity and an absence of (or very small number of) pinholes. Therefore, it was concluded that the WVTR results were reasonably representative of the coating barrier properties, and not artifacts due to sample defects.

Samples were tested for water holdout as described above. With all materials, the drops beaded up and no absorption of water was observed even after several minutes.

All samples were also tested for oil/grease resistance as described above. All the coatings obtained a rating of 12 with the oil/grease resistance test, when tested on a portion of the sample free from mechanical coating defects (e.g., pinholes). Tests with a drop of corn oil produced the same results, with no absorption or penetration of oil.

The four materials with the best WVTR values (A, E, F, and G) were forwarded on for additional testing. These were subject to the in-house test for repulpability as described in the methods section. Of these, Materials A, F, and G showed repulpability comparable to the uncoated paper stock. Material E had remaining fragments of unpulped material, in sizes up to about 6 mm (in the longest dimension). Of the three materials with acceptable repulpability, Material A had the best WVTR values and was selected for further testing.

Pilot Coating

Samples of the base paper coated with Material A were prepared on the commercial coating line as described in the method section. Coat weight, solution solids content, and operating parameters were adjusted until the resulting coated product was substantially

TABLE 3. COATING WEIGHT AND WVTR OF PRODUCTION AND COMPARATIVE SAMPLES

Coating ID	lb/3,000 ft^2 (g/m^2)		Mils (microns) thickness	WVTR$^{(B)}$ g/(m$^2 \cdot$ d)
	Dry Weight Coated$^{(A)}$	Net Weight Coating		
CIS	50.8 (82.7)	10.8 (17.6)	4.8 (118.8)	19
C2S	54.3 (88.4)	14.3 (23.3)	4.8 (118.8)	16
Polycoated	59.6 (97.0)	19.6 (31.9)	5.3 (131.3)	17
Waxed paper	19.2 (31.3)	??? (???)	1.3 (32.5)	163

(A)Coating weight includes barrier coating and VCI for C2S and polycoated.
(B)WVTR measured at 73 °F (23 °C), 50% RH.

free of coating defects (streaks or pinholes as detected by application of vegetable oil to the surface). The resulting one-side coated (C1S) material was tested for WVTR, water, and oil resistance. The C1S material was then put through the coating process a second time to apply VCI to the other side (to make the C2S material). The C2S product was tested again for WVTR. It was also subject to the standard corrosion inhibiting tests (vapor inhibiting ability [VIA], steel razor blade, copper razor blade), and received a passing score on all tests.

The WVTR results of the CIS and C2S products, along with some comparison materials, are shown in Table 3.

Conclusions

It is shown by the data presented in this article that it is feasible to produce repulpable VCI paper with water vapor barrier properties very close to that of polycoated paper, and much better than a commercial waxed paper. Further, these are produced by application of a single coat of waterborne coating solution, making them cost competitive with polycoated paper. It is expected that with further optimization of the coating formulations, the barrier properties could be further improved to be equal to or even superior to those of polycoated paper. While there appeared to be distinct differences in WVTR properties of the specific formulations, obtaining a defect-free continuous coating was critical to high WVTR performance. The viscosity of Formula A was higher than the others and may have been a significant factor in achieving the desired coating uniformity under industrial coating conditions.

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Water-Based Coatings Powered by Nanoparticle Vapor Corrosion Inhibitors

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Today's waterborne coatings are steadily fulfilling several requirements that are usually met by solvent-borne systems, such as good adhesion, corrosion resistance, and improved weathering. Aqueous technologies are generally preferred over their solvent-based counterparts due to ease of application, lower volatile organic compounds, and cost. However, waterborne coatings still have limitations in providing long-term protection for metals in extremely corrosive environments. Through research it has been found that combining nanoparticle vapor phase corrosion inhibitors (NANO-VCIs) with a non-zinc environmentally friendly metal complex inhibitor will significantly improve the long-term corrosion protection of acrylic paints on steel substrates. This article investigates the use of NANO-VCI technology with a non-zinc environmentally friendly metal complex inhibitor to greatly improve the long-term corrosion protection of an acrylic coating applied direct to metal.

New international environmental regulations have led to a global trend in developing coatings that are environmentally friendly. Some of these eco-friendly coatings contain only nontoxic, non-reportable raw materials that are safe to humans and/or the environment.

In this study, it has been found that the use of a nontoxic inorganic corrosion pigment combined with nanoparticle vapor phase corrosion inhibitor (NANO-VpCI®[†] [VCI]) technology in a waterborne acrylic protective direct-to-metal (DTM) coating produced a synergistic anti-corrosion effect compared to using these inhibitors separately.

Corrosion inhibitors work by two primary methods. They can either absorb or coat a metal surface, protecting it from corrosive environments, or they may react chemically with a metallic element to form a non-reac-

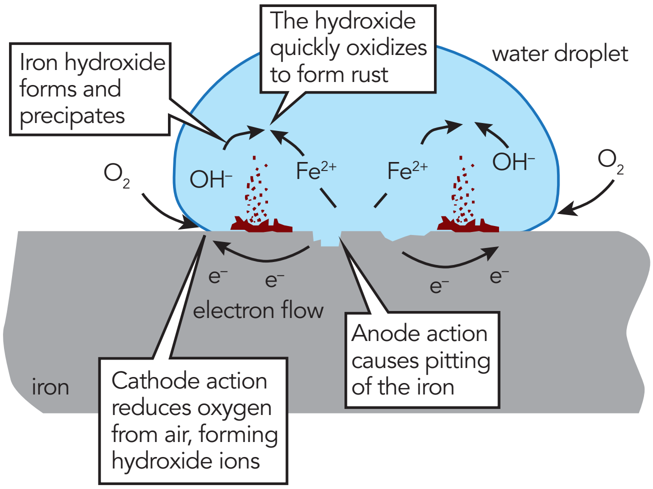

FIGURE 1. Electrochemical cell action driven by the energy of oxidation continues the corrosion process.

[†] Trade name.

tive, hydrophobic (passive) layer that prevents the mechanism of corrosion to the metal substrate. To be effective, an inhibitor should interact with the anodic or cathodic sites (retarding the oxidation and reduction corrosion reactions) along with shielding water from the metal surface and preventing it and other corrosive electrolytes from coming in contact with the bare metal.

Oxidation Reaction of Iron

For steel to corrode, oxygen and water must be in direct molecular contact with the surface of the substrate (Figure 1). The anodic and cathodic reactions are shown in Equation (1):

$$\begin{aligned} &\text{Anodic:} && Fe(s) \rightarrow Fe^{2+}(aq) + 2\,e- && (1)\\ &\text{Cathodic:} && O_2 + 2\,H_2O + 4e- \rightarrow 4\,OH- &&\\ & && H+ + e- \rightarrow \tfrac{1}{2}\,H_2(g) &&\\ & && M_2+ + 2\,e- \rightarrow M(s) && \end{aligned}$$

For this experiment, a nontoxic metal-inhibiting pigment was used to provide passivation and ion scavenging protection. The inhibitor works through hydrolysis by dissociating and reacting with Fe^{2+} and OH^- ions to form $Fe(PO_4)$ and $X(OH)_x$; both molecules then precipitate to build a passive micro-phobic layer on the metal surface. The inhibiting pigment also acts as an ion scavenger, neutralizing corrosive species such as Cl^- and SO_4^{2-}, limiting their aggressive behavior toward metal corrosion (Figure 2).

However, although a good level of corrosion protection can be obtained with this one inhibitor, it is not perfect and due to its large particle size, gaps and voids exist between the pigment particles that are entry points for micro-corrosion that can expand and lead to coating failure (Figure 3).

To improve the corrosion performance of the coating, NANO-VCIs were added to the matrix. The blend of vapor phase corrosion inhibitors possesses the ability to penetrate and adhere to the metal surface under the gaps and micro-cavities providing a molecular layer of corrosion protection (Figures 4 and 5).

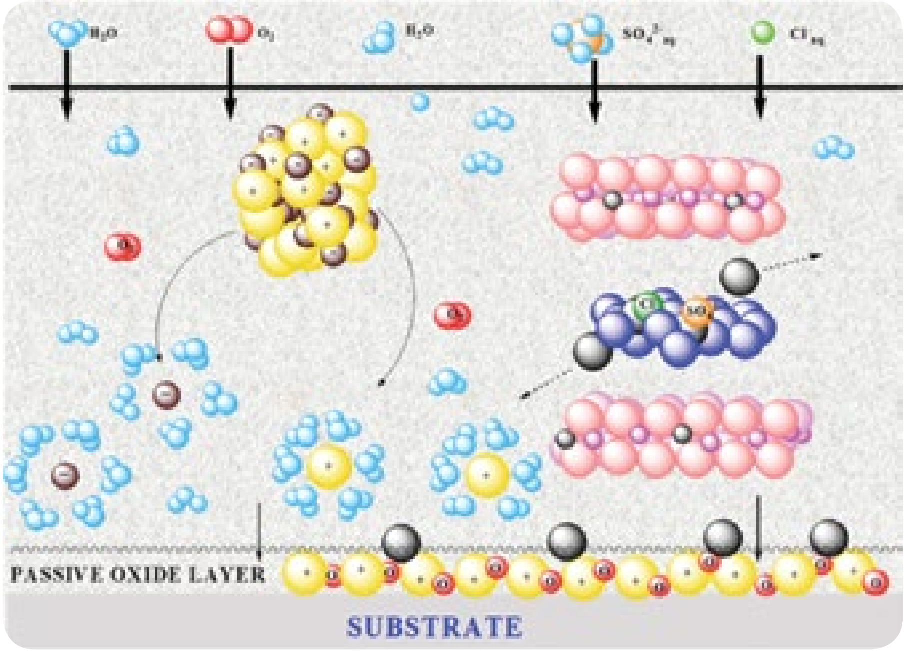

FIGURE 2. The reactions of an inhibiting pigment to provide passivation and ion scavenging protection.

The mechanism of the NANO-VCIs involves two parts; the first is the transport of the inhibitor to the metal surface and the second is how the inhibitor interacts on the metal substrate to form a film. When added to a liquid coating, the inhibitors in this study react with water and dissociate. After application, as the liquid coating cures, the charged inhibitors migrate and absorb onto the bare metal surface; adsorption occurs as a result of electrostatic forces between the electric charge on the metal and the ionic charges on 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; these non-reactive films can be absorbed onto passivating layers as well (Figure 6).

At higher concentrations, NANO-VCIs can also have a self-healing effect. If a fracture was to occur in a cured coating, the attractive forces of the inhibitor toward the exposed metal would cause them to migrate through the coating to the bare metal surface where they would then form a protective film. This technology is being used mostly in temporary coatings due to their softer films and low abrasion resistance.

The combination of the NANO-VCI with a nontoxic metal complex inhibitor pro-

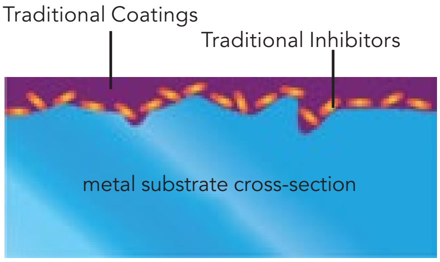

FIGURE 3. The large particle size of a traditional inhibitor can lead to micro-corrosion and eventual coating failure.

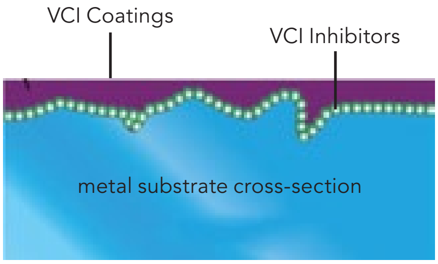

FIGURE 4. Metal substrate cross-section with VCI coatings and VCI inhibitors.

FIGURE 5. The blend of VCIs provides a molecular layer of corrosion protection.

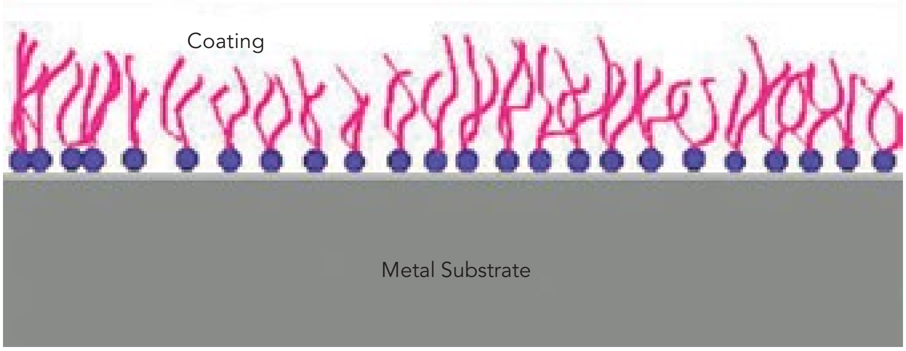

FIGURE 6. Tails of the inhibiting molecules produce a film that repels water.

FIGURE 7. Control sample, 540 h of continuous salt spray.

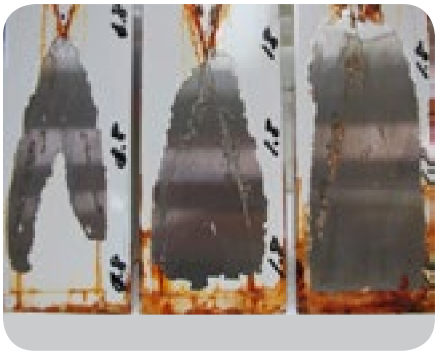

FIGURE 8. Close-up of Figure 7.

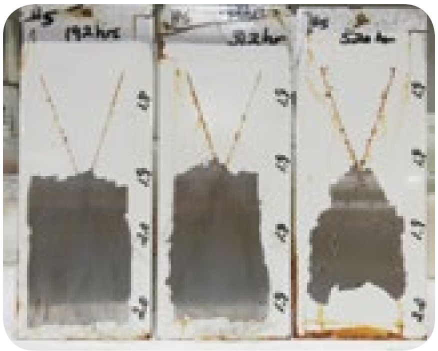

FIGURE 9. Sample containing ecologically friendly pigment inhibitor.

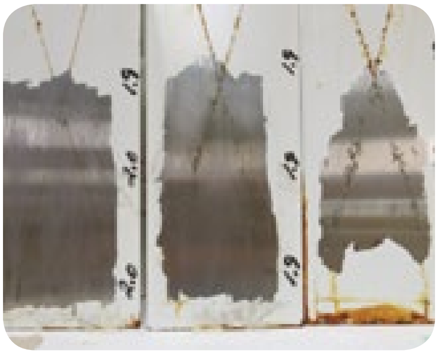

FIGURE 10. Close-up of Figure 9.

FIGURE 11. Sample containing NANO-VCI and ecologically friendly pigment inhibitor.

FIGURE 12. Close-up of Figure 11.

duced a great improvement in corrosion resistance from the synergy between the two through passivation, ion scavenging, and protective film formation.

Experimental Procedure

This study examines three self-crosslinking acrylic latex coating samples with and without the corrosion inhibitors. All samples were made using a high-speed mixer with a cowles blade.

Each coating sample was then applied to three separate CRS SAE 1010 (4 by 12-in [102 by 305-mm]) panels using a wire wound drawdown rod to produce ~2.0 mils of dry film thickness. The carbon steel specimens were prepared in accordance with ASTM B117[1] salt spray testing method.

After reaching full cure (seven days at ambient temperature), the panels were scribed as explained in method ASTM D1654.[2] All backs and edges of the panels were taped to prevent corrosion creep. They were then placed into a 5% sodium chloride (NaCl) salt fog chamber for environmental testing for up to 520 h. After 520 h, each sample was rinsed, scraped, and rated for creep (ASTM D1654), blistering (ASTM D714[3]), and degree of rusting (ASTM D610[4]). Photos were taken after testing.

Results

The main goal of the experiment was to improve the corrosion resistance of a coating through the synergy between the combination of NANO-VCI with an eco-friendly inhibiting pigment. Normally this type of long-term corrosion prevention is done by using inhibitors that are toxic and dangerous such as lead, zinc, and chromates. However, good long-term performance was achieved from the synergy of the two inhibitors mentioned in this study.

The result in Figure 7 presents the poor performance of an acrylic water-based paint with no inhibitors other than for flash rust. The paint failed ≤192 h in the salt chamber (failure ≥ 3-mm creep from scribe). The salt vapors were able to quickly penetrate the film's barrier, which leads to blistering and loss of adhesion and causing the underlying substrate to corrode (Figure 8).

The results in Figure 9 show the coating made using only the nontoxic metal complex inhibitor. As can be seen, the overall corrosion resistance was greatly improved. The film displays a much lower level of red rust on its surface, with just a slight level of blistering near the scribes; the effectiveness of the pigment in improving passivation and ion-scavenging is clearly demonstrated. However, even though the addition of the inhibitor improved the overall corrosion resistance, the coating failed ≤520 h in the salt spray chamber (Figure 10).

Figure 11 shows the results for the sample containing both the NANO-VCI and ecologically friendly pigment inhibitor that passed 520 h. The addition of the VpCI clearly complemented the corrosion resistance of the coating by reducing the level of blistering and substrate corrosion that was seen with just the metal complex inhibitor alone. This again was done by the ability of the VCI to migrate underneath the microgaps and voids that exist between the pigment particles and attach itself to the metal substrate to form a protective passivating film; there is an obvious synergy between the two inhibitors (Figure 12).

Conclusions

Today's waterborne coatings are steadily fulfilling several requirements that are usually met by solvent-borne systems, making aqueous technologies preferred over their solvent-based counterparts for environmental regulation and safety reasons.

Through research it has been found that combining NANO-VCIs with a nontoxic metal complex inhibitor will significantly improve the long-term corrosion protection of acrylic paints that are applied directly to metal. The combination of these inhibitors provides a synergetic multi-layer defense of corrosion resistance through passivation, ion-scavenging, and film formation.

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