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2004 *F.N. Speller Award Lecture:* Efficacy of Vapor Phase Corrosion Inhibitor Technology in Manufacturing

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ABSTRACT

Corrosion is a plight that faces everyone who works with metals. Its impact on the U.S. economy has been documented to be about 4% of the gross national product. It was estimated that about one third of the corrosion damage could be avoided. The avoidable costs were related to the failure to use the best practices available. There are several ways of combating corrosion. One way that is gaining wider acceptance is to use vapor phase corrosion inhibitors. Volatile corrosion inhibitors were originally developed to protect boilers and piping systems of ships to be mothballed. Their effectiveness and ease of application attracted early users. Over the years, the field of usage has increased to cover electronics, packaging, process industries, reinforced concrete, coatings, and metalworking fluids.

KEY WORDS: vapor phase corrosion inhibitors, manufacturing, metals

INTRODUCTION

A 2002 NACE International study estimated that the annual cost of corrosion in the United States alone nears 3.1% of the gross domestic product (GDP)—a staggering $340 billion. The real-world implication to metal manufacturing and processing is the added cost of doing business. Aside from the most visible effects, such as product failure and rejection, are those "hidden" costs that are part of the everyday manufacturing process. Expenditures on cleaning, blasting, reworking, and disposal combined with labor-intensive additional processing steps greatly affect the bottom line.

To combat the devastating effects of corrosion and in an attempt to preserve valuable military equipment, the U.S. Navy tested the first volatile corrosion inhibitor (VCI) chemistry for the mothballing of boilers and similar structures on war ships in the late 1940s. The core chemistry at that time was a toxic amine nitrite solution applied to the inside of inaccessible spaces. Although a similar nitrite-based chemistry is still widely used today, there is an effective, environmentally sound, and safer alternative. (Figure 1).

A new generation of corrosion inhibitors emerged in the late 1970s called vapor phase corrosion inhibitors (VCIs). These new chemistries were developed to utilize state-of-the-art, nontoxic organic inhibitors in a wide variety of forms. The VCI technology, as described below, protects metals from corrosion during manufacturing, processing, shipping, storage, and while in use without any residual contamination to the protected metal. The result is a vast line of products all designed to take the cost of corrosion out of the metalworking and manufacturing process.

CORROSION AND VCIs

Simply defined, corrosion is the natural process of a material, usually a metal, returning to its original state through an electrochemical process due to a reaction with the surrounding environment. Al-

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Toxicity Data

Chemical	LD50 (mg/kg-rat)
Table salt (sodium chloride)	3,000
Food preservative/corrosion inhibitor (sodium nitrite)	85
Nitrite-based VCI powder	284
Non-nitrite-based VCI powder	2,100

FIGURE 1. *Toxicity data for some common corrosion inhibitors.*

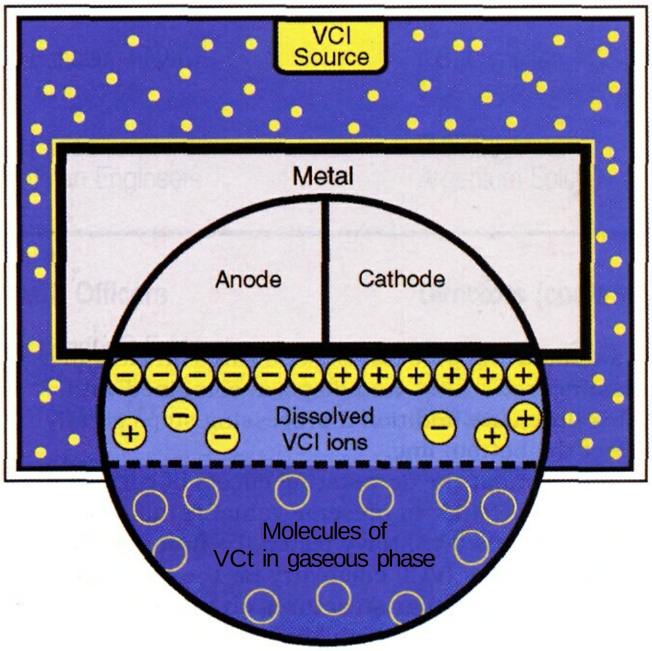


FIGURE 2. *VCI molecules vaporize, condense on all metal surfaces, and re-heal and self-replenish through further condensation of the vapor.*

though corrosion is a natural process, certain atmospheric conditions that a metal is exposed to during its manufacture, processing, storage, or shipment can aggressively accelerate the degradation. Most notable of these factors are sulfur dioxide (typically associated with the burning of coil, oil, and gas), acids in packaging materials, and temperature and humidity fluctuations during transit.

VCIs are organic compounds that have sufficient vapor pressure under ambient atmospheric conditions to travel essentially to the surface of the metal by diffusion and to adsorb physically onto the surface. In the presence of moisture, the VCI molecule becomes polarized and attracted to the anode and cathode of the metal. Once the VCI protective ions are adsorbed onto the surface, the electrochemical process of corrosion is interrupted as the ions create a protective barrier to contaminants such as oxygen, water, chlorides, and other corrosion accelerators. With the protective barrier in place, the corrosion cell cannot form and corrosion is halted. (Figure 2).

Unlike nitrite inhibitors, which do not have sufficient vapor pressure under ambient conditions, VCI products can actually protect yellow and ferrous metals as well as soldered parts and alloys. Whereas water-displacing, water-absorbing, dehumidification, and barrier products try to alter an ever-changing environment surrounding the metal, VCI technology passivates the metal's surface. In fact, VCI molecules actually use the same mechanism that accelerates corrosion to accelerate the release of protection molecules—a built-in defense mechanism (Figure 3).

MANUFACTURING WITH VCI PRODUCTS

During the typical manufacture of a metal product, the material is cleaned, oiled, blasted, machined, finished, assembled, painted, and packaged—in some cases, numerous times before it is sent to the customer. By effectively utilizing the benefits of VCI technology, many of these in-process steps can be completed eliminated (Figure 4). Other cost savings result when the disposal and cleanup costs are calculated. Imagine a manufacturing process where the starting metal structure is processed without need for secondary oil rust preventatives, rework, rust removal, blasting, or cleaning.

VCIs in their pure form are usually off-white powders and can be used in this form for protection of large void spaces (such as the heat recovery steam generators [HSRGs], boilers, turbines, and pipes previously coated with amine nitrite inhibitors). Additionally, VCIs can be incorporated into coatings, greases, functional fluids, cleaning systems, hydrotesting solutions, even concrete and plastics. The result for a manufacturer utilizing VCI product is streamlined processes, improved product quality and acceptance, and overall cost reduction.

But how do VCI molecules affect the metal surface? The VCI molecules are designed specifically to prevent reactions on the metal surface. Whereas many methods of corrosion protection alter the metal (i.e., stainless vs carbon steel, cathodic protection, and treatment of metal), VCIs do not alter the surface as the protective ions are adsorbed to the surface rather than becoming permanently attached.

A study was conducted on VCI products to determine how the protective molecules affected the exposed ends of fiber optics cables. Three products were tested, including VCI-treated anti-stat polyethylene film, polyurethane foam impregnated with VCI, and VCI powder contained in high-density vapor permeable polyethylene film pouches. The testing showed that there was no indication of attenuation change caused by the corrosion inhibitors. The results of this study are included in Figure 5.

Corrosion Prevention Methods Used by Military Organizations

Corrosion Prevention Method	Product Type	Benefits	Disadvantages
Water-displacing products	Petroleum-based (light oils or thixotropic greases)	• Relatively inexpensive • Water displacement • Create a barrier coating on metal surfaces • Excellent permanent protection	• Costs increase with additives (e.g., contact inhibitors, extreme-pressure additives) needed to enhance protection • High labor and material costs for application and removal of product • Use of solvent-based cleaners for product removal makes these products unsafe for the worker and environment
Water-absorption products	Silica gel (dessicants)	• Economical alternatives for temporary protection • Effective for storage and shipping • Effective in electronic and electrical operations	• Difficult to calculate specific moisture that will be present (i.e., requires more dessicant and inspection) • Costs increase with the addition of more dessicant and inspections • Airtight seal is required but difficult and expensive to achieve
Dehumidification	• Dehumidifier • Vapor barrier bags	• Can be successful if air flow to the metal is totally restricted • Vapor barrier bags are excellent for one-time use (offer a sturdy multilayer film) • Good way to protect electronics	• Dehumidifier > Electricity mandatory for dehumidifier and not available in remote locations > Difficult to keep a seal on the metal object > High cost of equipment and associated upkeep • Vapor barrier bags > High costs of materials and labor needed to create air-tight protection > Not a good method to use during operations
VCIs	• Anodic inhibitors (e.g., sodium nitrite [$NaNO_2$], dicyclohexylamine nitrite, sodium benzoate) • Cathodic inhibitors • Mixed inhibitors	• Anodic inhibitors > Prevent metal corrosion • Cathodic inhibitors > Slow cathodic reaction > Precipate onto cathodic sites, restricting diffusion of corrosive species • Mixed inhibitors > Adsorbed onto metal surface, creating a monomolecular layer > Monomolecular film acts as a buffer, maintaining pH at optimum range for corrosion resistance > Provide a universal effect on corrosion process	• Anodic inhibitors > Negative effect on worker safety > Negative effect on environment

FIGURE 3. *Advantages and disadvantages of different methods of preservation utilized by military organizations.*

PROVING VCI EFFECTIVENESS

While there are many methods to test corrosion inhibiting compounds and methods, the industry standards involve three principle criteria—contact protection, vapor protection, and protection in simulated environments. There are standardized and industry-accepted tests for each.

First, will the compound inhibit corrosion when it is in direct contact with the metal it is designed to protect? The "Razor Blade" test is a quick laboratory test with a pass or fail rating—if corrosion exists after the set time frame, the product fails. This test essentially tests the contact corrosion inhibiting ability of a material. In most cases, the test is conducted on test coupons and on multiple types of metal.

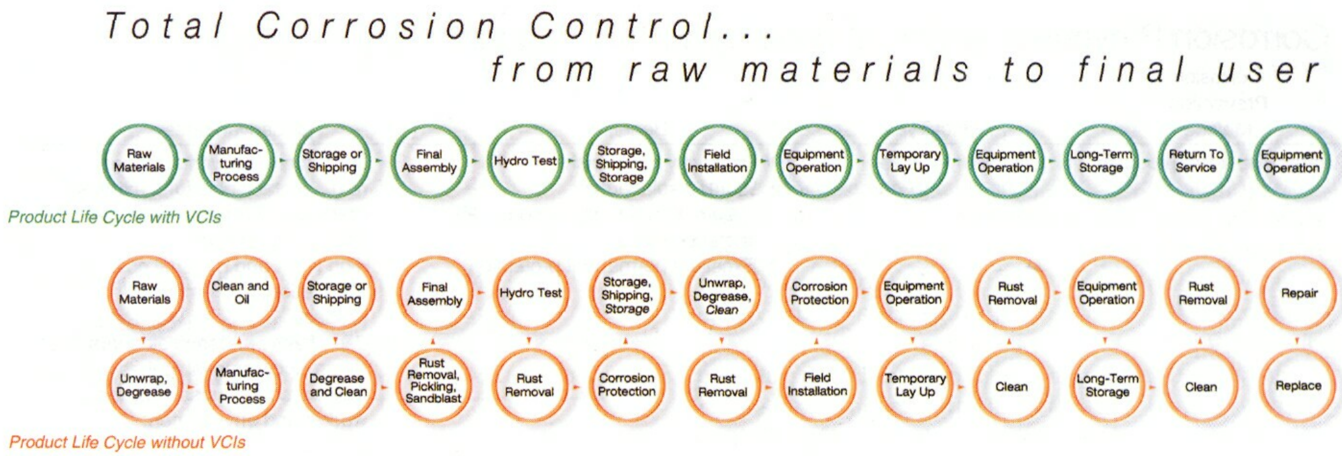
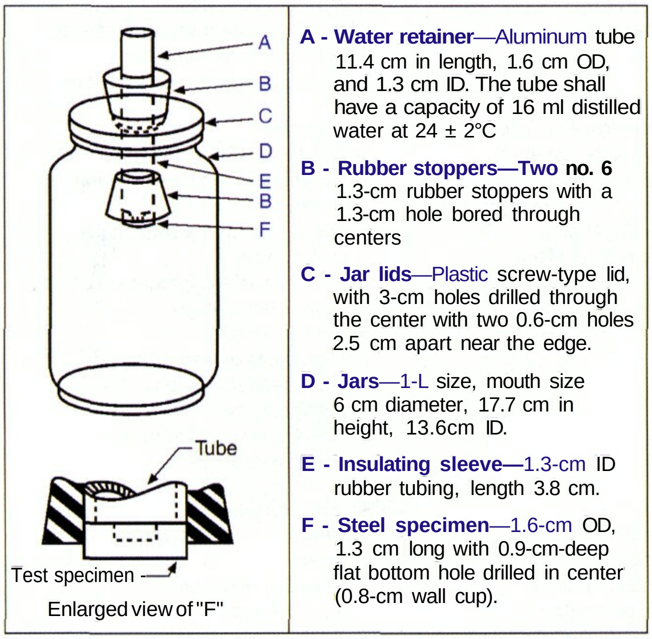
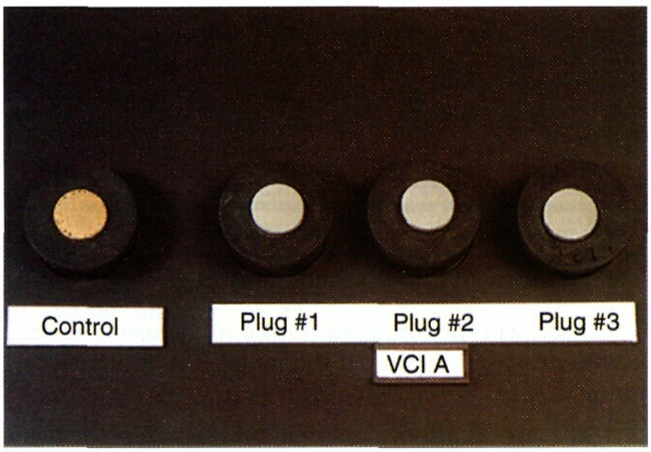


FIGURE 4. *Flow charts for manufacturing that utilizes and does not utilize VCI coating compounds.*



(a)



(b)

FIGURE 5. *(a) Standard setup for Federa! Standard 101c, German VIA test, (b) Results of the Federal Standard.*

Second, Federal Standard 1O1c, the German VIA test, is used to determine if a corrosion inhibiting compound will protect a metal when the compound is never in contact with the metal. For this test, the corrosion inhibiting compound is placed in a glass jar. A metal slug is placed in a rubber gasket attached to the lid, so it is prevented from coming in contact with the corrosion-inhibiting product.

Figure 5 details the results of the German VIA test for polyethylene film containing VCI for multimetal protection compared to a nitrite-based flexible packaging film. The results are measured on a scale from 0 to 3 (0 = worst protection, 3 = best protection), which detail the severity of corrosion on the metal plug. Since nitrite-based inhibitors lack sufficient vapor pressure under ambient conditions, the products typically do not pass the German VIA test, nor does the corrosion inhibitor travel to the metal.

Rochester Institute of Technology conducted extensive testing on several VCI products including nitrite-based technologies used by Daubert, Northern Technologies, Aicello, SKS, as well as barrier film produced by Intercept and non-nitrite VCI products manufactured by Cortec Corporation. The results of these tests are shown in Figure 6.

Simulating environments through ASTM D 1748 Humidity, ASTM Bl 17 Salt Fog, and ASTM D 53 Prohesion also can be an effective means of evaluating the comparative corrosion protection ability of VCI products. These tests accelerate the corrosion process by placing the metal samples (either coupons or actual parts) in environmental chambers where atmospheric conditions are monitored and altered. Figure *7* details the comparative results of several VCI products under these tests (Figures 7[a] through [c]).

Many VCI products also have industry approvals for use in highly restrictive markets, such as direct and indirect food contact. Polyethylene film contain-

Sample #	Manufacturer	Pass/Fail	Data
Films			
1	Cortec Corp.	Pass	Clear
2	Daubert Corp.	Fail	Discoloration and corrosion
3	Northern Instruments (Zerust)	Pass	Clear
4	Brangs & Heinrich	Fail	Severe discoloration
5	Fuchs	Fail	Severe discoloration
6	Aicello	Fail	Discoloration
7	Intercept	Fail	Severe discoloration
8	SKS Corp.	Fail	Severe discoloration
Papers			
9	Brazil Paper	Pass	Clear
10	SKS Paper	Pass	Clear
11	Daubert Paper	Pass	Clear
12	Cortec Paper	Pass	Clear

(a)

Sample #	Manufacturer	Pass/Fail	Data
Films			
1	Cortec Corp.	Pass	Clear
2	Daubert Corp.	Fail	Severe discoloration
3	Northern Instruments (Zerust)	Fail	Corrosion and discoloration
4	Brangs & Heinrich	Fail	Corrosion and discoloration
5	Fuchs	Pass	Clear–slight discoloration
6	Aicello	Pass	Clear–slight discoloration
7	Intercept	Fail	Discoloration
8	SKS Corp.	Fail	Discoloration
Papers			
9	Brazil Paper	Pass	Clear
10	SKS Paper	Fail	Discoloration
11	Daubert Paper	Fail	Severe discoloration
12	Cortec Paper	Pass	Clear–slight discoloration

(b)

Sample #	Manufacturer	Pass/Fail	Data
Films			
1	Cortec Corp.	Pass	Minor discoloration
2	Daubert Corp.	Fail	Severe discoloration
3	Northern Instruments (Zerust)	Fail	Severe discoloration
4	Brangs & Heinrich	Fail	Severe discoloration
5	Fuchs	Pass	Minor discoloration
6	Aicello	Pass	Minor discoloration
7	Intercept	Fail	Severe discoloration
8	SKS Corp.	Fail	Severe discoloration
Papers			
9	Brazil Paper	Pass	Clear
10	SKS Paper	Pass	Clear–slight discoloration
11	Daubert Paper	Pass	Clear–slight discoloration
12	Cortec Paper	Pass	Clear–slight discoloration

(c)

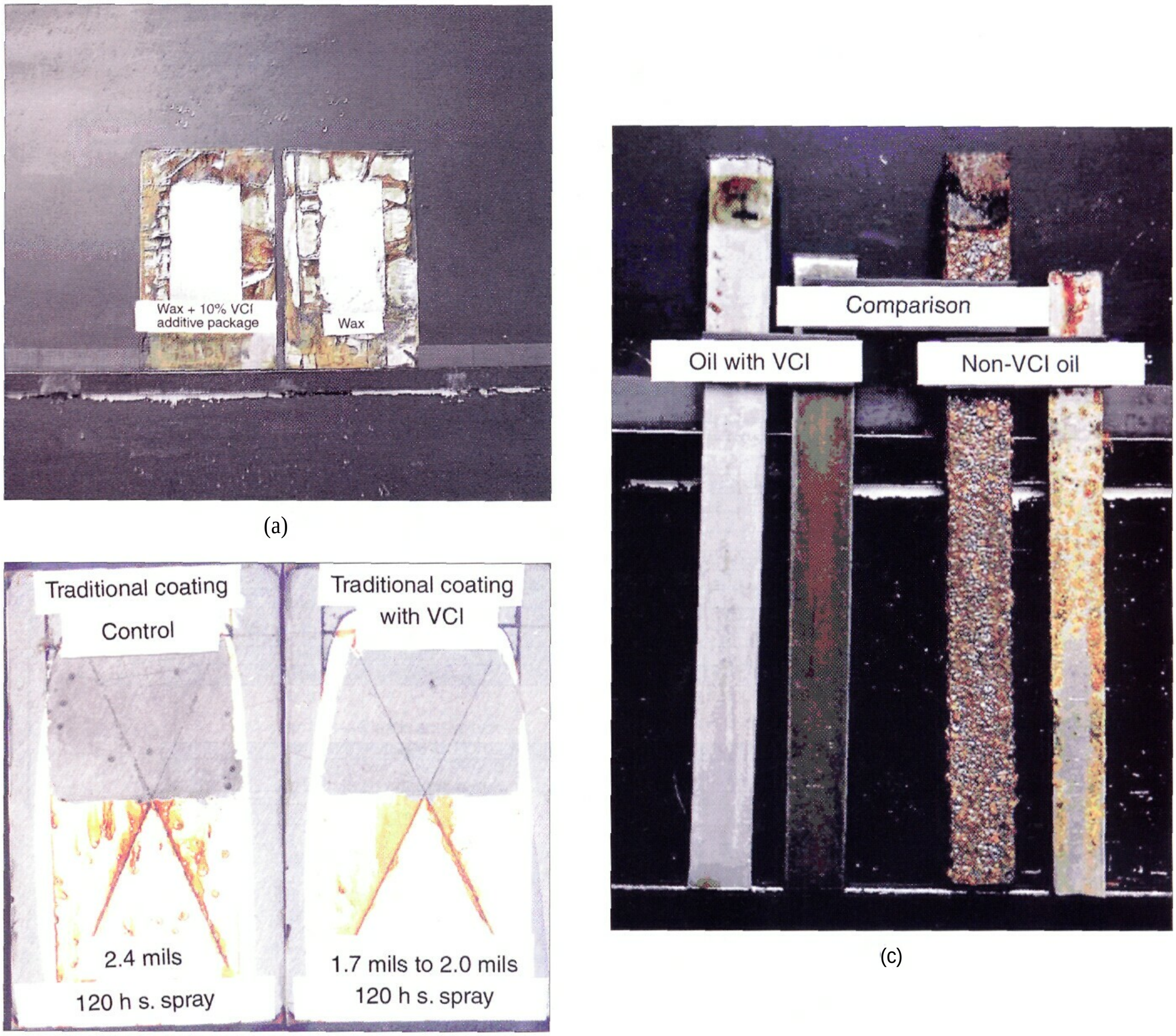
Sample #	Manufacturer		Grade	
Films				
1	Cortec Corp.		2	
2	Daubert Corp.		0	
3	Northern Instruments (Zerust)		2	
4	Brangs & Heinrich		0	
5	Fuchs		0	
6	Aicello		0	
7	Intercept		0	
8	SKS Corp.		1	
Papers				
9	Brazil Paper		2	
10	SKS Paper		3	
11	Daubert Paper		3	
12	Cortec Paper		3	

(d)

Product	Nitrite Based
Films	
Cortec Corp.	No
Daubert Corp.	No
Northern Instruments (Zerust)	Yes
Brangs & Heinrich	No
Fuchs	No
Aicello	Yes
Intercept	No
SKS Corp.	Not tested
Papers	
Brazil Paper	Yes
SKS Paper	Not tested
Daubert Paper	Yes
Cortec Paper	No

(e)

FIGURE 6. *Independent laboratory test results for: (a) carbon steel razor blade test, (b) copper razor blade test, (c) steel razor blade test, and (d) Federal Standard 101c, German VIA test, (e) Cross reference chart for nitrite vs non-nitrite VCI inhibitors.*



(a) (b) (c)

FIGURE 7. *(a) Wax, with and without VCI. Test according to ASTM V-117. (b) The addition of VCI materials to a traditional coating greatly improved performance in ASTM B-117. (c) ASTM B-117 testing of grease with and without VCI additive package.*

ing VCI for multimetal protection, for example, is ideally suited for the shipment and storage of food processing equipment and has indirect food contact approval from the U.S. Federal Drug Administration (FDA). Water-based temporary coatings containing VCI for multimetal protection has U.S. Department of Agriculture (USDA) approval for use on packaging material that is in direct contact with meat or poultry food products. Both approvals, as well as many others, are evidence that VCI technology can provide a cost-effective method of superior corrosion protection while remaining nontoxic, safe for workers, and without affecting the surface of the protected metal.

EXAMPLES OF VCI PRODUCTS IN USE

A large telecommunications equipment manufacturer was shipping high-value enclosures overseas using barrier film, desiccant, vacuum seal, and humidity cards yet they were still experiencing nearly 85% failure rate due to corrosion. Not only was their packaging and rust preventative method extremely expensive, an even higher cost was borne when the equipment had to be replaced. Additionally, the packaging was compromised when customs offers were forced to open the barrier film to inspect the enclosures.

Initial shipments were established using only VCI emmitting devices (seen as the small green cup attached to the right side of the enclosure in Figure 8) and polyethylene film containing non-nitrite-based VCIs. This polyethylene film contains VCI molecules throughout the film and is translucent allowing easy customs inspection. The VCI emitting device quickly saturate the enclosure with the protective corrosion inhibiting vapor allowing rapid shipments.

After switching to VCI products, this manufacturer was able to eliminate all corrosion claims while reducing costs by nearly 60%, including a decrease in material and labor costs.

The U.S. Air Force also has effectively used VCI technology as part of its war readiness and equipment preservation methods. Vehicles that previously would have taken nearly a week to clean, drain, reassemble, and operate are now wrapped in co-extruded shrink film containing corrosion inhibitors, flame retardants, and UV inhibitors, with only the antenna and battery removed. All fluids in the vehicle, including brake, hydraulic, engine, and coolant, incorporate a VCI additive to the existing fluid. The VCI additive protects even after the oil or fluid has settled into the reservoir, as detailed in Figure 9.

A large Power Generation OEM manufactures their heat recovery steam generators (HRSGs) in South East Asia. Historically, these units would be

FIGURE 8. *A large piece of telecommunications equipment that was being packaged for shipment utilizing VCI technology.*

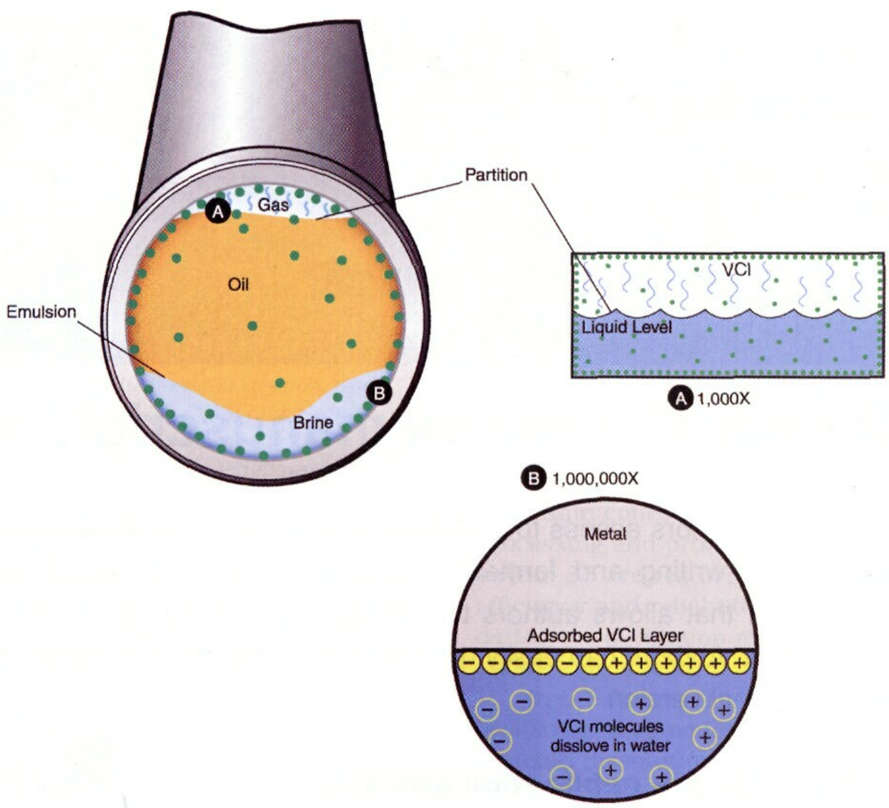


FIGURE 9. *Pipeline section showing active vapor phase corrosion inhibitors at the liquid phase, the vapor phase, the interface, and partition and emulsion barriers.*

full of corrosion upon arrival to their customer's site due to long shipping periods and large temperature and humidity fluctuations. Several years ago, they switched to VCI products to protect the high-value generators in transit as well as decrease cost and environmental impact.

United Space Alliance has utilized VCI technology successfully in the form of a water-based high-performance rust preventative for rocket booster structural components on National Aeronautics and Space Administration (NASA) rockets. The important factors for NASA included rust prevention, cleanliness, ability to topcoat, and the VCI product could not negatively affect the metal surface. The VCI coating is applied to virtually all space rocket booster (SRB) structural components and can be used for some limited flight applications.

CONCLUSIONS

❖ Corrosion costs industry billions annually and the effects on a manufacturing facility can be catastrophic if proper methods of prevention are not utilized. VCI products offer users an effective method of protection while maintaining strict adherence to product quality, environmental considerations, worker safety, and even throughput and the bottomline.