SPONSORED BY CORTEC CORPORATION

MP

A Supplement to

MATERIALS PERFORMANCE

CORROSION PREVENTION AND CONTROL WORLDWIDE

Environmentally Friendly Inhibitor Solutions

A Novel Approach to Tank Lining Coatings

Protecting Metals in Open-Loop Cooling Systems

Corrosion Inhibitors for the Petroleum Industry

Advances in Vapor-Phase Corrosion Inhibiting Coatings

NACE
INTERNATIONAL

MP MATERIALS PERFORMANCE
CORROSION PREVENTION AND CONTROL WORLDWIDE

EDITORIAL
DIRECTOR, PUBLICATIONS
MANAGING EDITOR
Gretchen A. Jacobson

TECHNICAL EDITOR
John H. Fitzgerald III, FNACE

STAFF WRITER
Kathy Riggs Larsen

EDITORIAL ASSISTANT
Suzanne Moreno

GRAPHICS
ELECTRONICS PUBLISHING SPECIALIST
Teri J. Gilley

MANAGER
E. Michele Sandusky

ADMINISTRATION
NACE EXECUTIVE DIRECTOR
Tony Keane

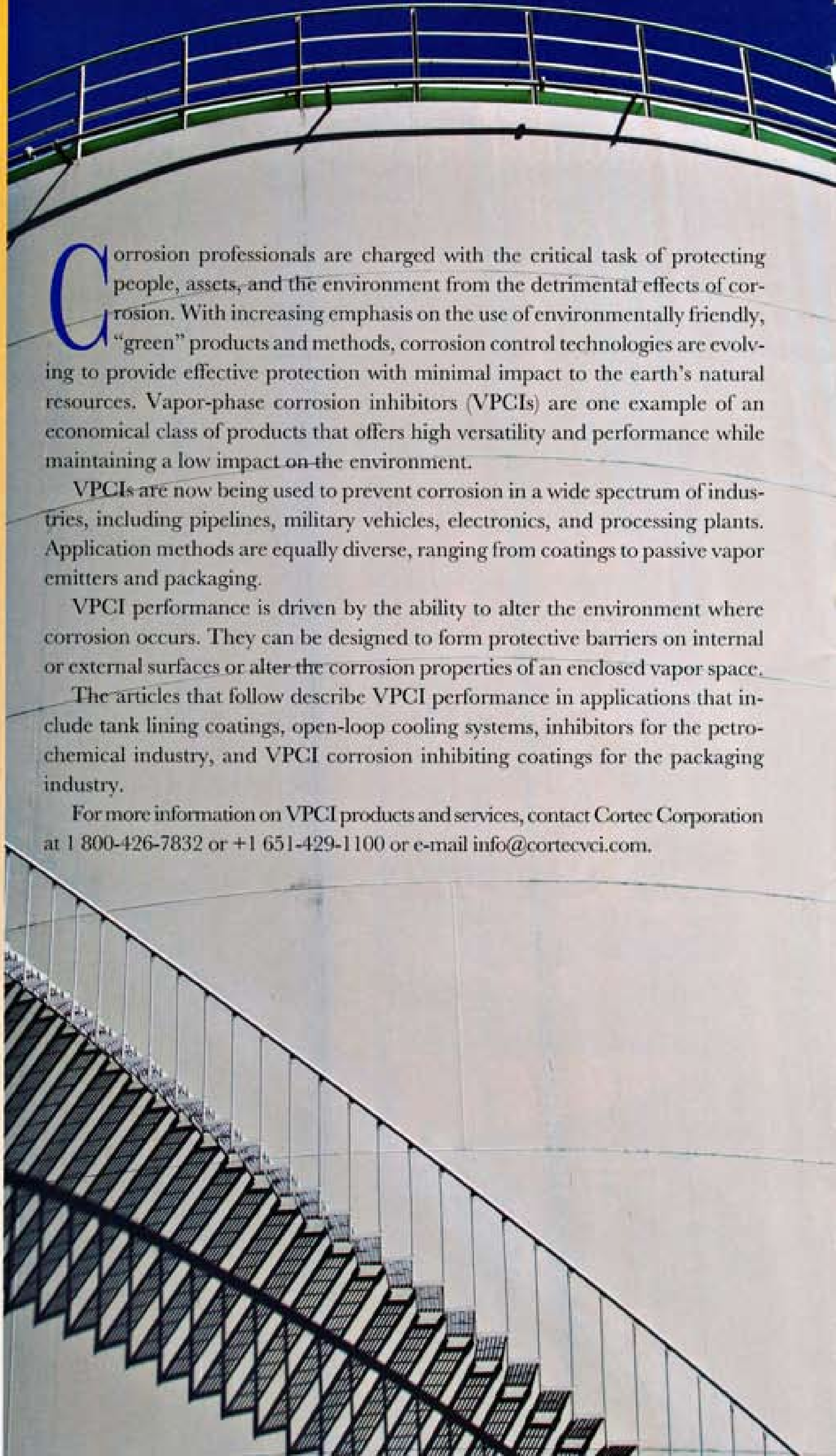
ADVERTISING
ACCOUNT EXECUTIVES
Anastasia Bisson
Corey Shaffer

ADVERTISING/BOOKS SPECIALIST
Brenda Nitz

REGIONAL ADVERTISING SALES REPRESENTATIVES
The Kingwill Co.
Chicago/Cleveland/New York Area–
+1 847-537-9196

NACE International Contact Information
Phone: +1 281-228-6200 Fax: +1 281-228-6300
E-mail: Firstservice@nace.org
Web Site: www.nace.org

Vapor-Phase Corrosion Inhibitors—The Green Way to Fight Corrosion



Corrosion professionals are charged with the critical task of protecting people, assets, and the environment from the detrimental effects of corrosion. With increasing emphasis on the use of environmentally friendly, "green" products and methods, corrosion control technologies are evolving to provide effective protection with minimal impact to the earth's natural resources. Vapor-phase corrosion inhibitors (VPCIs) are one example of an economical class of products that offers high versatility and performance while maintaining a low impact on the environment.

VPCIs are now being used to prevent corrosion in a wide spectrum of industries, including pipelines, military vehicles, electronics, and processing plants. Application methods are equally diverse, ranging from coatings to passive vapor emitters and packaging.

VPCI performance 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.

The articles that follow describe VPCI performance in applications that include tank lining coatings, open-loop cooling systems, inhibitors for the petrochemical industry, and VPCI corrosion inhibiting coatings for the packaging industry.

For more information on VPCI products and services, contact Cortec Corporation at 1 800-426-7832 or +1 651-429-1100 or e-mail info@cortecvci.com.

TABLE OF CONTENTS

4 **Anti-Corrosion Building Blocks for Open Loop Cooling Systems**
Andrea Hansen, Alla Y. Furman, Margarita A. Kharshan, and Elizabeth Austin, Cortec Corp.
This article shows the effectiveness of vapor-phase corrosion inhibitors (VPCIs) in protecting metals in open recirculating-loop cooling systems.

10 **A Novel Approach to Tank Lining Coatings**
Angel Green, Cortec Corp.; Chuck Ludwig, Universal Corrosion Specialist
A coating system featuring a low volatile organic compound-containing rust-converting water-based primer and a high-solids moisture-cure urethane coating is showing success for tank lining applications.

13 **Effectiveness of Petroleum Industry Corrosion Inhibitors Under Various Flow Conditions**
Boris A. Miksic, FNACE, Alla Y. Furman, and Margarita A. Kharshan, Cortec Corp.
New anti-corrosion additives have been formulated with VPCIs for internal protection of petrochemical facility piping and equipment, enhanced by their ability to self-replenish their mono-molecular protective layer.

18 **Advances in Environmentally Friendly Vapor-Phase Corrosion Inhibiting Coatings**
Kristy Gillette, Bob Berg, and Margarita A. Kharshan, Cortec Corp.
This article describes the advancement of VPCI-containing coatings that have permitted development of novel, environmentally friendly packaging products.

This publication contains a free bonus for its readers—a CD-ROM containing Cortec's complete *The Mothballing Handbook*. The manual provides systematic and documented procedures for temporary protection, lay-up, and mothballing of equipment, systems, and plants. It is organized for easy use and fast referencing by the classes of equipment you and your company need to protect. See p. 5 for your copy of this valuable resource.

Anti-Corrosion Building Blocks for Open-Loop Cooling Systems

Andrea Hansen, Alla Y. Furman, Margarita A. Kharshan, and Elizabeth Austin, *Cortec Corp., St. Paul, Minnesota*

Maintaining corrosion-free cooling systems in processing and manufacturing plants can be time consuming and costly. This article shows the effectiveness of vapor phase corrosion inhibitors (VPCIs) in protecting metals in open recirculating-loop cooling systems. VPCI materials can be made from biodegradable and sustainable resources. Laboratory test results, pilot test results, and field results are presented.

Cooling systems contain several types of metals including copper, steel, galvanized steel, and aluminum. Galvanizing, or applying a coating of zinc onto steel, is widely used in open-loop cooling systems for its cost effectiveness and ability to protect steel from corrosion. This material can offer 20 years or more life expectancy when maintained properly. When pH is over 8.2, however, corrosion may begin and "white rust" is seen. This oxidized zinc no longer protects the steel and the lifespan of the metal system would therefore be significantly reduced.[1]

Vapor-phase corrosion inhibitors (VPCIs) (Cortec Corp. trade name VpCI[†]) are one type of inhibitor that combat the corrosion problems faced by water-treatment providers. VPCIs have been used for a long time; however, some of them can be aggressive to non-ferrous metals, especially yellow metals.[2] In the majority of cases, corrosion protection of yellow metals is achieved by using triazole-based inhibitors. Their protection mechanism and effectiveness were studied by many researchers, but lately environmental regulations based on toxicity data have severely restricted the use of triazoles.[3]

Recent developments in VPCI technology prove that vapor corrosion inhibitors can be successfully utilized for the protection of multi-metal systems, including use in conjunction with water treatment. This topic will be discussed throughout this article.

Experimental Procedures

This experimental effort was designed to show the effectiveness of several VPCI building blocks to prevent corrosion to ferrous metals, and also white and yellow metals such as galvanized steel, zinc, aluminum, copper, and brass.

Experimental Materials

VPCI A is a synergistic blend of salts of carboxylic acids and alkalinity builders. It

Continued on p. 6

[†] Trade name.

The Mothballing Handbook

The CD-ROM below contains Cortec Corporation's complete guide for protecting plants and equipment during lay-up and mothballing. In the past, temporary corrosion protection was seldom needed but today, due to fluctuations in regulations and markets, the opposite is true. *The Mothballing Handbook* provides all the information you need for successful temporary corrosion control.

Continued from p. 4

contains triazole and can be used by itself or as part of a treatment to enhance protection against corrosion. VPCI B is a blend of salts of carboxylic acid and modified amide-based compounds with no triazole. VPCI C is a combination of vapor and contact corrosion inhibitors. The main ingredients are salts of amines and fatty acids with different chain lengths, and triazole is added for the protection of yellow metals. VPCI D is a blend of sequestering agents and the protein portion of soybeans. It consists of individual amino acids (protein's building blocks). The amino acids contain both a basic amino group (NH_2) and an acidic carboxyl group (COOH). Despite their relatively large size, the proteins spread into extremely thin films at an interface, exposing the reactive site of their amino acid chains.

Electrochemical Testing

Tests were performed in conditions based on recommendations of ASTM G5[4] using a potentiostat/galvanostat VersaSTAT[†] with a three-electrode system along with corrosion software model 352/252 SoftCorr[†] utilized for the electrochemical studies. Polarization curves were obtained at room temperature after at least 30-min immersion of the working electrode in the electrolyte.

The working electrode (made of zinc, steel, aluminum, or copper) was polished with 600-grit sandpaper, washed with methanol, and air dried for at least half an hour at room temperature.

Immersion and Partial Immersion Corrosion Tests

Tests were performed in conditions based on recommendations of ASTM G31.[5] Sanded and methanol-cleaned metal panels were immersed in containers filled with water-based solutions/electrolytes with added treatment or without it ("control"). After the test, the weight loss was determined or panels were visually evaluated for the presence of corrosion after cleaning according to ASTM G1.[6]

Tests in Pilot Cooling Tower

Various treatments were tested in the Model 005[†] cooling tower manufactured by RSD Towers. This unit provides 16 gpm (61 L/min) recirculation rate and has 1.5-in (38-mm) inlet and outlet piping. The test was performed in tap water with 2.3 to 2.5 cycles of concentration and a temperature of 45 to 50 °C. The pH of the system was between 8.6 and 8.8, the total dissolved solids in the basin were between 1,250 and 1,300 ppm, and the conductivity level was ~1,850 to 2,000 µS-cm.

Corrosion coupons were placed in contact with the water passing through the tower and corrosion rates were calculated using the average values from coupons and Equation (1).

$$\text{Corrosion rate} = (K \cdot W)(A \cdot T \cdot D) \qquad (1)$$

where $K = 3.5 \times 10^6$ (conversion factor to mpy), W = weight loss in grams, A = area in cm^2, T = time of exposure in hours, and D = density in g/cm^3.

Toxicity Testing

Primary Skin Irritation Test

The VPCI building blocks were applied to the skins of rabbits and secured with wrapping for a minimum of 4 h. Observations for skin irritation were conducted at 30 to 60 min after unwrapping as well as 24 h, 48 h, and 72 h. The sum of erythema and edema scores was calculated.[7-8]

Aquatic Toxicity Test

The VPCI building blocks were tested for aquatic toxicity with several species. These tests included 48-h static-renewal *Daphnia pulex* and *Pimephales promelas* definitive tests, which were performed in synthetic moderately hard freshwater according to EPA/600/4-90/027F[9] and 48-h static-renewal acute *Menidia beryllina* and *Mysidopsis bahia* definitive tests, which were performed in synthetic seawater according to EPA-821-R-02-012.[10] These tests yielded the No Observable Effect Concentration (NOEC) and Lowest Observable Effect Concentration (LOEC).

Results

The results of the laboratory testing of the VPCI building blocks are presented in the following tables and figures.

To compare the ability of VPCI A and D to protect copper, aluminum, and

TABLE 1

VPCI A corrosion rate data calculated from Tafel plots

Treatment	pH	Zinc Corrosion Rate (mil/y)	Protection Ability (%)
Control tap water	7.6	7.8	—
100 ppm VPCI A in tap water	7.8	1.06	86.5
Control calcium carbonate ($CaCO_3$) (1,000 ppm) solution	7.8	1.8	—
100 ppm VPCI A in $CaCO_3$ solution	7.9	0.24	87.2
Control calcium hydroxide $Ca(OH_2)$ solution	8.8	33.72	—
100 ppm VPCI A in $Ca(OH)_2$ solution	8.8	3.56	89.5
250 ppm VPCI A in $Ca(OH)_2$ solution	8.8	0.36	98.9
Control $Ca(OH)_2$ solution	9.6	91.14	—
50 ppm VPCI A in $Ca(OH)_2$ solution	9.6	26.79	70.6
250 ppm VPCI A in $Ca(OH)_2$ solution	9.6	5.14	94.4

TABLE 2

Average corrosion rate and protection ability results for VPCI A combined with conventional treatments

		CS	Galvanized Steel
Treatment	Average Corrosion Rate (mpy)	Protection Ability (%)	Protection Ability (%)
Control	15.98	—	—
Conventional Treatment 1	0.76	95.2	74.0
75% Conventional Treatment 1 + 25% VPCI A	0.35	97.8	94.3
Conventional Treatment 2	11.93	25.3	31.0
75% Conventional Treatment 2 + 25% VPCI A	2.23	86.0	94.0

TABLE 3

Results of linear polarization scans of formulations using VPCI A in combination with water treatment formulations

Treatment	CS Corrosion Rate (mpy)	Zinc Corrosion Rate (mpy)
Control (prepared solution)	22.0	11.50
170 ppm of Formulation 1 in prepared solution	8.17	6.84
170 ppm of Formulation 1 + VPCI A in prepared solution	3.52	5.87
150 ppm of Formulation 2 in prepared solution	7.47	4.625
150 ppm of Formulation 2 + VPCI A in prepared solution	5.34	2.99

galvanized steel against corrosion in static conditions, half immersion corrosion tests in tap water were performed. The data showed that the VPCI products outperformed their conventional counterpart in the protection of copper, aluminum, and galvanized steel. The coupons exposed to VPCI A and D exhibited no sign to slight sign of corrosion, whereas corrosion was found on the coupons exposed only to the conventional inhibitor.

Calcium salts are the most common minerals in water. It is known that waters with a high pH level cause corrosion of zinc and galvanized steel. To address the question of corrosion protection provided by VPCI A, an electrochemical test was performed.

The results depicted in Table 1 show that VPCI A provides a high level of corrosion protection for zinc in the presence of calcium carbonate ($CaCO_3$) and high pH level. Protection ability was calculated using Equation (2).

FIGURE 1

Galvanized steel coupons—control.

FIGURE 2

Galvanized steel coupons—formulation 1 + VPCI A at 170 ppm.

$$\text{Protection Ability (\%)} = \frac{\text{Corrosion Rate of Control} - \text{Corrosion Rate of Sample}}{\text{Corrosion Rate of Control}} \times 100 \qquad (2)$$

Results of immersion testing showed that VPCI A provides a high level of corrosion protection for carbon steel (CS) and galvanized steel when added to conventional water treatment formulas. The galvanized steel samples were in the solution for 10 days at 40 °C. Thereafter, corrosion products were removed by dipping for 15 s into 3% solution of hydrochloric acid (HCl) and weight loss was determinated[6] (Table 2).

Corrosion rates calculated from linear polarization scans (Table 3) are in agreement with the results of the immersion test, confirming that the addition of VPCI A improves the corrosion protec-

TABLE 4

Pilot cooling tower test results of formulations with and without VPCI D addition

Treatment	CS Corrosion Rate (mpy)	Protection Ability (%)	Galvanized Steel Corrosion Rate (mpy)	Protection Ability (%)	Copper Corrosion Rate (mpy)
Conventional 50 ppm + oxidizing biocide	1.3	79.5	2.5	44.3	0.051
VPCI D at 10 ppm + oxidizing biocide	0.9	85.5	0.77	82.9	0
Conventional + 10% VPCI D at 50 ppm (~5 ppm VPCI D) + oxidizing biocide	1.13	82.2	1.44	67.9	0.011

TABLE 5

Toxicity testing results of VPCI building blocks

Test	Species	VPCI A	VPCI C	VPCI D
Mammalian Toxicity Test 336 h	*Rattus sp.*	—	Theoretical LD_{50}>4,000 mg/kg rat	
Fresh Water Species 48-h static renewal test (EPA/600/4-90/027F)[13-14]	*D.pulex*	—	NOEC=10,000 ppm LOEC=>10,000 ppm	TBD
Fresh Water Species 48-h static renewal test (EPA/600/4-90/027F)[13-14]	*P. promelas*	—	NOEC=10,000 ppm LOEC=>10,000 ppm	TBD
Seawater Species 48-h static renewal test (EPA-821-R-02-012)[12,15]	*M. bahia*	NOEC=600 ppm CTS LEOC=1,000 ppm CTS	—	NOEC=360 ppm LOEC=600 ppm 48-h LC50=282 ppm
Seawater Species 48-h static renewal test (EPA-821-R-02-012)[12,15]	*M. beryllina*	NOEC=1,000 ppm CTS LOEC=2,500 ppm CTS	—	NOEC=<1,296 ppm LOEC=1,296 ppm 48-h LC50=2,630 ppm
Fathead Minnow[11]	Fathead Minnow	LC_{50}=1659 IC_{25}=141.2	—	—
Ceriodaphnia dubia[11]	*C. dubia*	LC_{50}=1051 IC25=86.7	—	—
Skin Testing[7-8]	Rabbit	0 at 4,000 ppm	0 at 2,000 ppm	—
COD, EPA method 410.1[16]	—	~81 ppm	—	—

tion of the water treatment formulations submitted.

Cooling tower testing commenced on conventional treatment TF1 with and without VPCI A at 250 ppm for one week, 100 ppm for one week, and then 50 ppm for six weeks to determine the protection of galvanized steel. This testing further confirmed that adding 25% of VPCI A to a conventional water treatment formulation lowered the corrosion rate of galvanized steel from 4.49 to 0.59 mpy. Figure 1 shows the control coupons and Figure 2 shows the coupons exposed to the combination of conventional treatment and 170 ppm VPCI A.

VPCI B was tested specifically as a replacement for triazole treatments used to protect copper. Protection ability was 99.65% for VPCI B, and 99.86% for triazole. Triazole is effective in corrosion protection of copper. Considering, however, that cooling systems usually include different metals, some of which (multi-metal systems) are not protected by triazole, it may be beneficial to use VPCI B, which can be used as a multi-metal corrosion inhibitor to protect all metals. This replacement for triazole is especially important as environmental issues become more stringent.

Another VPCI building block, VPCI C, was tested to show protection of a variety of metals. An immersion test was performed in tap water to show protection of copper/nickel alloy. VPCI C exhibited a protective ability of 80%.

Three more metals were used in the cooling tower to test the effectiveness of

VPCI C in a commercial formulation containing molybdates, tetraborates, triazoles, acrylic polymers, and phosphonates. The test ran the formulations at 250 ppm for seven days, 100 ppm for seven days, and 50 ppm for 80 days. Make-up water was also treated with 5 ppm of an oxidizing biocide. Results showed that by adding 10% VPCI C, there was additional corrosion protection to existing formulations.

A variety of metals were also used in cooling tower tests of VPCI D in conjunction with conventional water treatment products. Results in Table 4 show that VPCI D can be used alone to provide protection or can be added to formulations for additional corrosion protection.

The toxicity of VPCI building blocks to several species was tested to show that the VPCI building blocks are safe for handling and use in cooling water treatment programs. The recommended concentration for use remains safe for many species, allowing discharge according to local specifications. A summary of this testing is shown in Table 5.

Conclusions

According to the results of the immersion tests, polarization curves, and cooling tower tests, the VPCI building blocks provide corrosion protection for many types of metal when added to various water chemistries. They have been shown to be effective not only for ferrous metals, but also for the non-ferrous metals of aluminum, copper, and zinc, with some VPCI building blocks showing promising results as replacements for triazole-based products. The VPCI building blocks provide protection on their own and also when used in combination with conventional commercial treatments. Also, the recommended concentration for use remains safe for many species, allowing discharge according to local specifications.

This article is based on CORROSION 2009 paper no. 09484, presented in Atlanta, Georgia.

References

1 "White Rust: An Industry Update and Guide Paper," Assoc. of Water Technologies (2002).

2 H.H. Uhlig, R.W. Revie, *Corrosion and Corrosion Control* (New York, NY: John Wiley & Sons, Inc., 1985), p. 276.

3 N.M. Fillipov, D.A. Lawrence, "Developmental Toxicity of a Triazole Fungicide: Consideration of Interorgan Communication," *Toxicological Sciences* 62 (2001): pp. 185-186.

4 ASTM G5, "Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements" (West Conshohoken, PA: ASTM, 2004).

5 ASTM G31, "Standard Practice for Laboratory Immersion Corrosion Testing of Metals" (West Conshohoken, PA: ASTM, 2004).

6 ASTM G1, "Standard Practice for Preparing, Cleaning and Evaluating Corrosion Test Specimens" (West Conshohoken, PA: ASTM, 2003).

7 Lab Project #9693, ViroMED Biosafety Laboratories (2000).

8 Lab Project #10100, ViroMED Biosafety Laboratories (2000).

9 EPA/600/4-90-027F, "Methods for Measuring the Acute Toxicity of Effluents to Freshwater and Marine Organisms," 4th ed. (Washington, DC: EPA, 1993).

10 EPA-821-R-02-12-012, "Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms," 5th ed. (Washington, DC: EPA, 2002).

11 Project #341, Environmental Consulting & Testing (2008).

12 Environmental Enterprises USA, "48-hour Static-Renewal Acute *M. beryllina* and *M. bahia* Toxicity Test Results" (2001).

13 Environmental Enterprises USA, "48-hour Static-Renewal *Daphnia pulex* and *Pimephales promelas* Toxicity Test Results" (2001).

14 Environmental Enterprises USA, "48-hour Static-Renewal *Daphnia pulex* and *Pimephales promelas* Toxicity Test Results" (2008).

15 Environmental Enterprises USA, "48-hour Static-Renewal Acute *M. beryllina* and *M. bahia* Toxicity Test Results" (2008).

16 Maxim Technologies Inc. using EPA 600/4-79-020 "Methods for the Chemical Analysis of Water and Waste" (1999).

Andrea Hansen is a technical service engineer at Cortec Corp., 4119 White Bear Pkwy., St. Paul, MN 55110. She has worked at the company for four years, providing technical service for corrosion inhibition for the water treatment and construction industries.

Alla Y. Furman is a senior corrosion engineer at Cortec Corp. Her main work experience is in formulating and testing corrosion preventative products using various corrosion and electrochemical techniques. The products include water treatment, process additives, metal working, and concrete admixtures. She has a Ph.D. in engineering.

Margarita A. Kharshan is a laboratory director at Cortec Corp. She has developed and tested corrosion inhibitors for the last 14 years. She has more than 12 patents and has published numerous articles in different magazines. She has a Ph.D. from Moscow Lenin University.

Elizabeth Austin is a laboratory technician at Cortec Corp. She has been with the company for two years and has a B.S. degree in biology. *MP*

A Novel Approach to Tank Lining Coatings

Angel Green, *Cortec Corp., St. Paul, Minnesota*
Chuck Ludwig, *Universal Corrosion Specialist, Richmond, Texas*

Traditional tank lining coatings are costly, have high volatile organic compound (VOC) content, and generally require a high film thickness of multiple coats. This article presents the results of laboratory testing and field application of a new type of coating system applied to the inside of tanks exposed to corrosive environments. The coating system consists of a low-VOC rust-converting water-based primer and a high-solids moisture-cure urethane coating, which are applied at a much lower film thickness than the traditional tank lining coating systems.

The tank lining industry currently uses high-build tank lining systems made of heavy layers, consisting of several 8- to 10-mil (203- to 254-μm) coats of coal tar epoxies that do not contain corrosion inhibitors. These systems require sandblasting of the metal to NACE No. 2,[1] "Near White Blast Cleaning," before placing the spray-in liner at thicknesses up to 30 mils (762 μm).

Cortec Corp. has developed a low-VOC rust-converting water-based primer and a high-solids moisture-cure urethane coating system that yields a dry film thickness (DFT) of 5 to 7 mils (125 to 175 μm). The VOC content of the primer is 0.3 to 0.4 lb/gal (35.9 to 47.9 g/L) and the VOC content of the urethane coating is 3.1 to 3.2 lb/gal (371.5 to 383.5 g/L).

One comparative epoxy paint system would create an estimated 44.9 tons per year of VOC compared to the low-VOC system discussed here, which creates an estimated 1.86 tons per year of VOC. These amounts were determined by calculating the amount of product used per tank, based on two tanks coated per day.

To prove that the coating system can withstand the harsh environments, it underwent various accelerated weathering exposure tests in laboratory and field applications. This article describes the testing procedures and results, and presents the test conclusions.

Experimental Procedures

Test Criteria

The goal of the experimental effort was to replace the existing tank lining systems that are currently used in tanks holding hydrocarbon or high-salinity solutions with a better performing and environmentally sound coating system consisting of a low-VOC rust-converting water-based primer and a high-solids moisture-cure urethane coating.

Following are lists of the materials, methods, and procedures used in the tests.

Materials

- Low-VOC rust-converting water-based primer
- High-solids moisture-cure urethane coating

TABLE 1

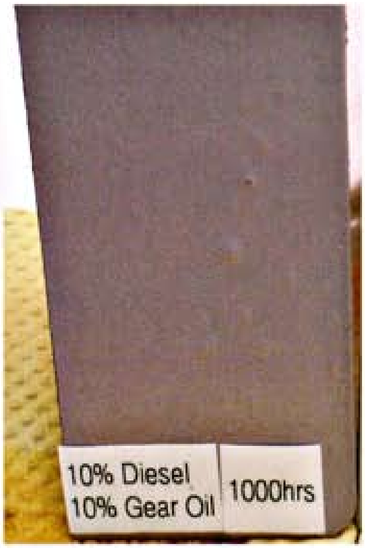
Immersion resistance results

Products	Chemical Immersed	Comments
Low-VOC rust-converting water-based primer with high-solids moisture-cure urethane coating (Figure 1)	Solution A 1,000 h	No effect to the coating
Low-VOC rust-converting water-based primer with high-solids moisture-cure urethane coating (Figure 2)	Solution B 1,000 h	No effect to the coating
Low-VOC rust-converting water-based primer with high-solids moisture-cure urethane coating (Figure 3)	Solution C 1,000 h	No effect to the coating

FIGURE 1

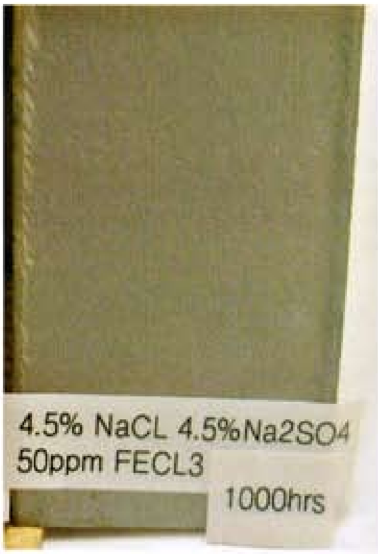
Panel immersed in Solution A. Low-VOC rust-converting water-based primer with high-solids moisture-cure urethane coating, 5 to 7 mils DFT.

FIGURE 2



Panel immersed in Solution B. Low-VOC rust-converted water-based primer with high-solids moisture-cure urethane coating, 5 to 7 mils DFT.

FIGURE 3



Panel immersed in Solution C. Low-VOC rust-converting water-based primer and high-solids moisture-cure urethane coating, 5 to 7 mils DFT.

- Diesel (Solution A)
- 10% diesel and 10% gear oil in water (Solution B)
- 4.5% sodium chloride (NaCl) and 4.5% sodium sulfate (Na_2SO_4) with 50 ppm iron chloride ($FeCl_3$) in water (Solution C)
- 1,600 ppm hydrogen sulfide (H_2S)
- Carbon dioxide (CO_2)
- 400 ppm sulfur dioxide (SO_2)
- 1010 carbon steel panels pre-rusted in salt spray and humidity cabinets (ASTM B117[2])
- Minitest[†] 500 (DFT detector)
- Wet film thickness gauge

Methods

- Visual inspection
- ASTM B117 salt spray testing

Coating Procedures

1. The low-VOC rust-converting water-based primer was applied to the pre-rusted panel by brush at a wet film thickness of 3 to 5 mils.
2. These panels were then air dried in ambient conditions for 24 h.
3. Next, the panels were coated with the high-solids moisture-cure urethane coating at a wet film thickness of 3 to 4 wet mils (100 µm).
4. The wet film thickness was checked by using a wet film gauge.
5. All of the coated panels that were tested in this work were coated as noted above.

Immersion Resistance Testing Procedures

Coated panels were air dried in ambient conditions for 48 h and then immersed in two hydrocarbon solutions, Solution A and Solution B, as well as the high-salinity Solution C. The panels were evaluated at various intervals for signs of corrosion and coating deterioration.

Gaseous Environment Testing Procedures

One coated panel was air dried in ambient conditions for 168 h, and then exposed to the gaseous environments in the following order, for time indicated and evaluated at various intervals:

1. CO_2 testing—first, the prepared panel was placed inside a jar con-

---

[†] Trade name.

TABLE 2

Gaseous environment test results

Products	DFT	Gas	Comments
Low-VOC rust-converting water-based primer with high-solids moisture-cure urethane coating	4.2 to 4.5 mils (105 to 112.5 μm)	72 h CO_2 24 h SO_2 (400 ppm) 24 h H_2S (1,600 ppm)	Panel had slight condensation and the color darkened after H_2S

FIGURE 4

Gaseous environment test panel. Low-VOC rust-converting water-based primer and high-solids moisture-cure urethane coating, 4.2 to 4.5 mils DFT.

taining a cup of water. The jar was closed and CO_2 was injected into the water for 72 h.

2. SO_2 testing—second, the prepared panel was placed into a 1-gal (3.785-L) glass jar containing a solution to create a 400-ppm sulfur dioxide (SO_2) environment, per the CC-003 test.[3]
3. H_2S testing—finally, the prepared panel was placed into a 1-gal glass jar containing a 50-mL beaker with 0.02 g of $FeCl_3$. Next, 0.5 mL of 1 N hydrochloric acid (HCl) was added to the 50-mL beaker to create a 1,600-ppm H_2S environment. The jar was closed and electrical tape was applied around the lid before the jar was placed into a 50 °C oven for 24 h, per the CC-009 test.[4]

Results of Laboratory Testing

Immersion Resistance Testing

For the coating system to be accepted as an alternative for tank linings, 1,000 h of immersion testing in the listed chemicals had to be run and passed.

Table 1 and Figures 1 through 3 show the results of the immersion resistance testing. No negative effects were seen on the coating during this testing.

Gaseous Environment Testing

Table 2 and Figure 4 show the results of the gaseous environment testing.

Field Applications

In August 2006, holding tanks containing either the high-salinity solution or a hydrocarbon solution were coated with the low-VOC rust-converting water-based primer and the high-solids moisture-cure urethane coating system according to the following steps:

1. Remove the man-way hatch and bolts and ensure proper ventilation before entering.
2. Spray heavy-duty alkaline cleaner/degreaser diluted with water on all weld seams, as well as all collars and hatches.
3. Power-wash the entire tank from ceiling to floor, including the man-way hatch. Continue by mopping and drying out the tank for the next step.
4. Apply the low-VOC rust-converting water-based primer by brush, pushing it into all weld seams, collars, doors, and openings.
5. Roll out the ceilings, walls, and floor with the primer, starting from the top and finishing with the floor, back-rolling to ensure even application. The coating should be applied at 3 to 5 wet mils thickness. Allow the coating to dry for 12 h. It should appear black and glossy. If the coating does not appear black and glossy, apply a second coat.
6. Apply the high-solids moisture-cure urethane by brush, pushing it into all weld seams, collars, doors, and openings.
7. Roll out the ceilings, walls, and floor with the urethane, starting from the top and finishing with the floor, back-rolling to ensure even application. The coating should be applied 3 to 4 wet mils thick. Allow the coating to dry for 12 h. It should appear dull silver.

Results of Field Application

Observations of the field applications made in 2008 showed that the coating system protected the tanks from corrosion for the last two-year test period. There were only minimal signs of corrosion observed at the two-year point.

Conclusions

Laboratory and field measurements show that the coating system of a low-VOC rust-converting water-based primer and a high-solids moisture-cure urethane coating conforms to the performance criteria for tank lining systems containing hydrocarbon and/or high-salinity solutions.

References

1 NACE No. 2/SSPC SP-10, "Near-White Blast Cleaning" (Houston, TX: NACE International).

2 ASTM B117, "Standard Method of Salt Spray (Fog) Testing" (West Conshohocken, PA: ASTM).

3 Cortec Corp. Work Instruction CC-003, "SO_2 Test Method" (St. Paul, MN: Cortec Corp.).

4 Cortec Corp. Work Instruction CC-009, "H_2S Test Method" (St. Paul, MN: Cortec Corp.).

This article is based on CORROSION 2009 paper no. 09488, presented in Atlanta, Georgia.

Angel Green is a coatings chemist at Cortec Corp., 4119 White Bear Pkwy., St. Paul, MN 55110. She has 13 years of experience developing industrial coatings and has been with Cortec Corp. for more than three years, with one patent pending. She is secretary of the Northwestern Society for Coatings Technology (NWSCT) and has been a member of NWSCT and the National Paint and Coatings Association/Federation of Societies of Coatings Technology (NPCA/FSCT) since 2006.

Chuck Ludwig is vice president of Sales and Development, Universal Corrosion Specialist, 1117 FM 359, Ste. 140, Richmond, TX 77406. He has 30 years of experience in the oil and gas financial area and four years of working with Cortec as a distributor and applicator of the products. He is a four-year member of NACE. *MP*

Effectiveness of Petroleum Industry Corrosion Inhibitors Under Various Flow Conditions

Boris A. Miksic, FNACE, Alla Y. Furman, and Margarita A. Kharshan,
Cortec Corp., St. Paul, Minnesota

Several types of corrosion inhibitors were tested at the concentration range of 50 to 200 ppm in an electrolyte and electrolyte-hydrocarbon mixture in the presence of carbon dioxide (CO_2) and hydrogen sulfide (H_2S) with and without flow modifiers. The obtained results show that tested corrosion inhibitors are effective in the studied range of flow rates and are compatible with flow modifiers.

Utilization of corrosion inhibitors is currently the most common method of protecting against corrosion in all petrochemical facilities in the world. The optimal combination of drag reducers (flow enhancers) and corrosion inhibitors provide end users with an effective way of increasing oil production and significantly prolonging the life of pipelines. Drag reduction is a physical phenomenon in which friction decreases in turbulent flow through pipelines. It leads to increased fluid flow or reduced pressure loss. Chemicals that can affect drag reduction—drag-reducing agents (DRAs)—have oilfield application mainly in crude oil transportation and water reinjection lines.[1-3]

The new anti-corrosion additives were formulated utilizing vapor-phase corrosion inhibitors (VPCIs) (Cortec Corp. trade name VpCI[†]). Unlike conventional inhibitors, such as amine-based filming corrosion inhibitors, an injection of VPCI-based material into any part of the system will set the VPCI to work immediately with a self-replenishing monomolecular protective layer.[4-5] VPCI technology can be used in pipelines, oil and gas wells, refinery units, and fuels. In addition, these VPCI-based anti-corrosion additives have been designed to work well in multiphase flow systems in conjunction with different drag reducers.

The different combinations of corrosion inhibitors and drag reducers provide systems with improved water flow and corrosion protection for pipelines carrying water or a mixture of hydrocarbon and water. All of these lead to energy savings in oil production and increased overall recoverable reserves. The reduction of operating pressure will, in turn, bring about a lower back pressure in the well head and lead to additional oil production, enabling a substantial annual revenue increase. The formulations of corrosion inhibitors and drag reducers were specifically designed to be effective in pipelines carrying either fresh water, seawater, or produced water; or in multiphase systems with a continuous water phase. In many aging oil fields, the

---

[†] Trade name.

amount of water increases over time to the point where a water-soluble drag reducer/corrosion inhibitor is needed instead of an oil soluble product.

The work discussed in this article is a continuation of a study of VPCIs for the petrochemical industry.[4-5] It presents two VPCI products used in conjunction with two DRAs: VPCI A corrosion inhibitor, which contains drag-reducing ingredient DR1 in its formulation, and VPCI B corrosion inhibitor, which is used in conjunction with drag reducer DR2 as a two-part system. This system can be applied using two pumps in the same line for continuous treatment.

Experimental Materials

Several classes of substances have been found to have drag-reducing properties; among these are quaternary ammonium salts (DR1) and anionic polymers (DR2).[1-3] The chemical nature of VPCI A and VPCI B is very similar—they both are based on fatty acid imidazoline chemistry. This group of imidazolines has a very low solubility in the water phase, which is commonly increased by using them in conjunction with acetic acid (CH_3COOH) (AA). However, AA adds solubility only and does not provide additional corrosion protection.[4] That is why the long chain organic acid was used in the formulations of VPCI A and VPCI B.

Fatty Acid Imidazoline

The fatty acid imidazoline consists of the following: an imidazoline, a long hydrocarbon tail group, and a short pendent group. According to S. Ramachandan,[6] the best corrosion protection is provided by imidazolines containing the ethylamino group as a pendent group and a fatty acid radical (hydrocarbon tail) containing not lower than C15. This kind of imidazoline was used in our work and will be further named as a fatty acid imidazoline (FAI).

Organic Acids

The long-chain organic acids were chosen for a new formulation based on our knowledge of their film-forming properties: Dimer acid (DA) combined with a small amount of AA was used in the formulation.

Vapor-Phase Inhibitors

Aminocarboxylates were used in the formulation to provide protection in the vapor phase. VPCI A contains DR1. This compound is based on quaternary amines, from the class of the salt of aromatic heterocyclic compounds. VPCI B additionally contains a cosolvent that provides good compatibilities with VPCI B and DR2. This is important based on the requirement of single dosing systems.

Steel Test Panels

Test panels (625 mm^2) were made from SAE 1010 steel.

Testing Protocol

The testing protocol was based on the recommendations of ASTM G170[7] and NACE International Publication 1D196.[8] Corrosion protection properties were tested in the electrolyte: 9.62% sodium chloride (NaCl), 0.305% calcium chloride ($CaCl_2$), 0.186% magnesium chloride hexahydrate, and 89.89% de-ionized water.

Static Tests

Static tests were made in sweet and sweet/sour conditions in an oven at 70 °C for 48 h using the following procedure:

- Electrolyte was purged with CO_2 or nitrogen (N_2) for 1 h. When CO_2 was used, the resulting pH level was 4.5. H_2S at a concentration level of 500 mg/L was generated in the sealed system by adding 1,700 mg/L of AA and 3,530 mg/L sodium sulfide ($Na_2S \times 9\ H_2O$). Kerosene K-1 was used to simulate the hydrocarbon phase. Tests were performed on panels or electrodes made from SAE 1018 carbon steel (CS).
- The weight loss of the panels was determined and corrosion rate/percent protection calculated.

TABLE 1

Results of static corrosion test in sweet conditions

Sample ID	Start Weight (g)	End Weight (g)	Difference (mg)	Z,% of Corrosion Protection
Control	22.0295	21.9362	–93.3	—
50 ppm VPCI A	22.0289	22.0157	–13.2	85.8
100 ppm VPCI A	21.6107	21.6040	-6.7	92.8
50 ppm VPCI B	22.1844	22.1779	-6.5	93.0
100 ppm VPCI B	21.3372	21.3344	-2.8	96.8

TABLE 2

Results of static corrosion test in sweet/sour conditions

Material	Start Weight (g)	End Weight (g)	Difference (mg)	Z, % of Corrosion Protection[A]
VPCI A, 50 ppm	21.0804	21.0782	-2.2	97.9
VPCI B, 50 ppm	21.3788	21.3771	-1.7	98.4
VPCI B, 50 ppm + DR2, 50 ppm	21.7324	21.7308	-1.6	98.5
Control[B]	20.5388	20.4343	–104.5	—

[A] $Z = 100\% (C_c - C_i)$: C_c = corrosion rate without inhibitor; C_i = corrosion rate with inhibitor.

[B] No inhibitor.

TABLE 3

Results of the electrochemical dynamic corrosion test in electrolyte purged with CO_2

Material	Corrosion Rate, mpy x 10^{-3}[A]		Z, % of Corrosion Protection[B]	
	500 rpm	2,000 rpm	500 rpm	2,000 rpm
VPCI A, 50 ppm	15.24	45.81	92.6	87.3
VPCI B, 50 ppm	17.62	47.33	91.1	86.9
VPCI B, 50 ppm + DR2, 50 ppm	13.60	31.38	93.4	91.3
Control[C] (no drag reducer)	206.0	360.7	—	—

[A] Surface area of the coupon is 62.5 cm².

[B] $Z = 100\% (C_c - C_i)$: C_c = corrosion rate without inhibitor; C_i = corrosion rate with inhibitor.

[C] No inhibitor.

Dynamic Tests

Dynamic tests were performed using the same electrolyte and hydrocarbon mixture as in the static tests, with continuous purging of CO_2 at a temperature of 70 °C. The potentiostat VersaSTAT[†], manufactured by EG&G Princeton Applied Research Co., and the Rotating Cylinder Electrode[†], manufactured by Pine Instruments, were used for the electrochemical testing. The effect of the flow on corrosion inhibition was studied at the rotating rate of 500 to 3,000 rpm. The corrosion rate was determined by analyzing the polarization curves obtained by the linear polarization technique. The corrosion rate of the unprotected electrode was measured after 1 h of immersion; then the inhibitor or inhibitor and drag-reducing compound was added. The corrosion rate was measured after 6 h of testing.

Vapor Corrosion Inhibition

The vapor-inhibiting ability (VIA) was evaluated by testing according to the VIA and H_2S procedures.

VIA was performed as follows: One gram of the inhibitor was introduced into the quart jar. The jar was sealed with a CS sample attached inside. After conditioning at room temperature for 2 h, a 3% solution of glycerin in de-ionized water was added into the jar. The jar was again sealed and placed in the oven at 40 °C for 2 h. After the test jar was opened, the condition of the CS samples were examined and provided protection rated according to Federal Test Method 101C.[9]

The H_2S test was performed as follows: One gram of the inhibitor in a small dish and a panel made from SAE 1010 steel were placed into a 1-gal (3.785-L) jar. The jar was sealed and conditioned for 20 h. H_2S was then generated in the jar by combining 0.02 g of iron sulfide (FeS) and 0.5 mL of 1 N hydrochloric acid (HCl) in a small beaker. The jar was placed in an oven set for temperature cycles of 8 h at ambient and 16 h at 50 °C. The panels were inspected for the presence of corrosion after one cycle in the oven.

[†] Trade name.

TABLE 4

Results of the dynamic corrosion test in electrolyte purged with CO_2

Material	Corrosion rate, mpy x 10^{-3}(A)		Z, % of Corrosion Protection(B)	
	2,500 rpm	3,000 rpm	2,500 rpm	3,000 rpm
VPCI B, 50 ppm + DR2, 50 ppm	89.71	150.6	84.2	78.3
VPCI B, 75 ppm + DR2, 50 ppm	23.28	51.36	95.9	92.6
Control(C) (no drag reducer)	567.8	694.1	—	—

(A)Surface area of the coupon is 62.5 cm^2.

(B)$Z = 100\% (C_c - C_i)$: C_c = corrosion rate without inhibitor; C_i = corrosion rate with inhibitor.

(C)No inhibitor.

TABLE 5

VIA and hydrogen sulfide test results

	VIA			H_2S
Sample ID	Plug #1	Plug #2	Plug #3	
VPCI A	Grade 3	Grade 3	Grade 3	No corrosion
VPCI B	Grade 3	Grade 3	Grade 2	No corrosion
Control	Grade 0	N/A	N/A	Corrosion

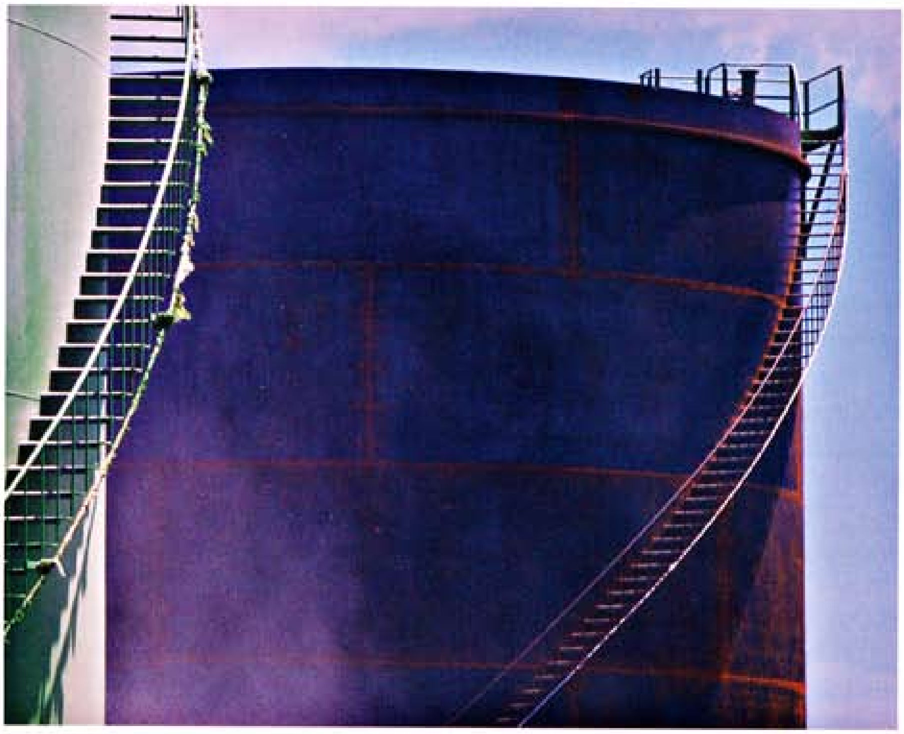
Grade 1: Minute corrosion inhibiting effect (note: there is no Grade 1 in the table), Grade 2: Medium corrosion inhibiting effect, Grade 3: Good corrosion inhibiting effect.

TABLE 6

Vortex test results(A)

Material	Initial Data	Time to Close the Vortex (s)		
		10 Min After Mixing	2 h After Mixing	24 h After Mixing
DR2	28	—	—	—
VPCI B + DR2 (1:1)	—	32	32	32

(A)The mixture of DR2 and VPCI B did not harden one week after the two products were mixed.



Vortex Test

This test was used to evaluate the drag-reducing ability of DR2 and its combination with VPCI B. The vortex test was performed using the follow procedure: 500 mL of water was poured into a 1-L beaker and stirred at ~500 rpm. Then 4 g of DR2 or 8 g of 1:1 mixture of VPCI B and DR2 was added into the vortex using a syringe. The time lapse until the vortex closed was determined.

Results

The results of the static corrosion tests are presented in Tables 1 and 2. All three types of treatment—VPCI A, VPCI B, and the combination of VPCI B and DR1—show effective corrosion protection with sweet (Table 1) and sweet/sour (Table 2) electrolyte in the presence of hydrocarbons. Corrosion rates were almost equal in the case of the VPCI B and its combination with DR2. This confirmed that DR2 does not affect the inhibiting ability of VPCI B in static conditions and does not prevent the adsorption of the inhibitor on metal surfaces.

Tables 3 and 4 present the results of the testing in dynamic conditions.

Table 3 shows that the corrosion rate is low in all three cases when the rotation rate is 500 rpm. Increasing the rotation rate causes an increase in corrosion rate. At the same time, the combination of VPCI B and DR2 provides better corrosion protection than VPCI A and VPCI B separately under elevated rotation-rate conditions. By further increasing the rotation rate, the corrosion rate increased. Nevertheless, the increased corrosion rate can be suppressed by increasing the concentration of the corrosion inhibitor.

Table 5 shows the results of the vapor corrosion inhibition ability of VPCI A and B. The data show that studied inhibitors emit the molecules into the surrounding atmosphere, providing corrosion protection against the oxygen, moisture, and H_2S in gaseous form.

Table 6 presents compatibility data of VPCI B and DR2. Data show that drag reducer DR2 does not lose it effectiveness when combined with VPCI B.

The mixture of VPCI B and DR2 did not visibly change after one week of mixing. This fact confirms that the transporting pipelines can be treated with the two-part system VPCI B and DR2 through the joint feeding system.

Conclusions

VPCI A and VPCI B are effective corrosion inhibitors in sweet/sour electrolyte-containing hydrocarbons. The effectiveness of VPCI A and VPCI B depends on the flow rate. Increased concentration is necessary to suppress corrosion when the flow rate is high.

According to the test results, VPCI A and B provide vapor corrosion inhibition.

DR2 is compatible with VpCI B and enhances the protective ability of VPCI B under high flow rate.

References

1 G. Schmit, "Drag Reduction—a Widely Neglected Property of Corrosion Inhibitors," proc. of 9th European Symposium of Corrosion and Scale Inhibitors, 2000.

2 S. Xueming, L. Jianzhong, "Experimental Research on Drag Reduction by Polymer Additives," http://fluid.power.net/techbriefs/hanghzau/5_2_5.pdf.

3 "Molecule Shows Promise as a Drag Reducer and Corrosion Inhibitor," Baker Petrolite Supplement to *MP*, February 2001.

4 M. Kharshan, A. Furman, "Incorporating Vapor Corrosion Inhibitors (VCI) in Oil and Gas Pipeline Additive Formulations," CORROSION/98 paper no. 236 (Houston, TX: NACE International).

5 B.M. Miksic, M.A. Kharshan, A.Y. Furman, proc. of 10th European Symposium of Corrosion and Scale Inhibitors, 2005.

6 S. Ramachandan, B.L. Tsai, M. Blanco, H. Chen, Y. Tang, W.A. Goddard, *Langmuir* 12 (1996): p. 6419.

7 ASTM G170, "Standard Guide for Evaluating and Qualifying Oilfields and Refinery Corrosion Inhibitors in the Laboratory" (West Conshohocken, PA: ASTM).

8 NACE International Publication 1D196, "Laboratory Test Methods for Evaluating Oilfield Corrosion Inhibitors" (Houston, TX: NACE).

9 Fed. Test Method Std. No. 101C, "Test Procedures for Packaging Materials."

This article is based on CORROSION 2009 paper no. 09573, presented in Atlanta, Georgia.

Boris A. Miksic, FNACE, is president and chief executive officer of Cortec Corp., 4119 White Bear Pkwy., St. Paul, MN 55110. He has served in this capacity for 32 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 F.N. Speller Award for longtime contributions to corrosion engineering. A NACE Fellow, he has been a NACE member for more than 35 years.

Alla Y. Furman is a senior corrosion engineer at Cortec Corp. Her main work experience is in formulating and testing corrosion preventative products using various corrosion and electrochemical techniques. The products include water treatment, process additives, metal working, and concrete admixtures. She has a Ph.D. in engineering.

Margarita A. Kharshan is a laboratory director at Cortec Corp. She has developed and tested corrosion inhibitors for the last 14 years. She has more than 12 patents and has published numerous articles in various magazines. She has a Ph.D. from Moscow Lenin University. MP

Advances in Environmentally Friendly Vapor-Phase Corrosion Inhibiting Coatings

Kristy Gillette, Bob Berg, and Margarita Kharshan,
Cortec Corp., St. Paul, Minnesota

Coatings for substrates used in the packaging industry have undergone a substantial transformation with the push to promote environmentally friendly products. This change of direction has transcended from non-renewable materials derived from fossil fuels to bio-based renewable resource-derived products. This article discusses the advancement of environmentally friendly vapor-phase corrosion inhibitor (VPCI)-containing coatings that have permitted development of novel VPCI packaging products.

Environmentally friendly water-based coatings for paper provide a packaging alternative to petrochemical-based products. Grease- and water-resistant corrosion inhibiting papers can be produced using environmentally friendly products. Grease-resistant papers are often based on perfluorochemicals (PFCs) or wax-based products, both of which have adverse environmental impacts, and statewide banning of these products is currently under review.[1] Waxed papers are not repulpable, which contributes to environmental issues and increased waste. Water-based emulsions with natural co-binders has permitted development of a bio-based and biodegradable grease-resistant paper that provides corrosion protection for oiled or dry parts during storage, transit, or overseas shipment. Moisture barrier papers have been produced utilizing similar green chemistry. These products are 100% repulpable and recyclable.

There exists, however, many packaging applications where paper is not suitable and more durable materials like films must be used. Recent advances in bio-based and biodegradable polymers have helped ease the reliance on petrochemicals, reducing the carbon footprint. Where petrochemical-based materials must be used, water-based coatings aid in the reduction of hazardous waste. These approaches have led to adhesive films like vapor-phase corrosion inhibitor (VPCI) (Cortec Corp. trade name VpCI[†]) masking film and VPCI cohesive film.

An environmentally friendly VPCI cohesive film that will bond only to itself, and not the metal parts wrapped within, has been developed. The coating contains aqueous corrosion inhibitors and natural rubber latex rather than synthetic rubbers that are produced from petroleum derivatives. Applying this coating to both traditional and bio-based film substrates provides protection from corrosion and mechanical damage. Since the film adheres to itself, it doesn't leave any residue behind, allowing the parts packaged within to be corrosion free and ready for use.

[†] Trade name.

Anti-skid linerboard can also be constructed from non-hazardous materials. This paper is used to prevent slippage of stacked products during shipment and storage and the addition of VPCIs offers corrosion protection.

Incorporating VPCI chemistries into a water-based pressure-sensitive adhesive provides a non-hazardous coating solution for both traditional and modern films. Using a water-based acrylic adhesive rather than a solvent-based product has several environmental and safety advantages. The masking film provides corrosion protection, while protecting metal surfaces from scratching or marring.

Experimental Procedures

Functional Properties Tests

Grease-Resistant Paper

The performance of the grease-resistant paper was assessed by TAPPI T454[2] and the 3M Scotchban Test Kit[†]. Although the test kit was designed to test PFC-based products, it provides a good measure for grease and solvent resistance and has been adapted under TAPPI UM 557[3] and TAPPI T559.[3] The test comprises 12 test solutions that vary in aggressiveness as the ratios of castor oil, toluene ($C_6H_5CH_3$), and heptane [$CH_3(CH_2)5CH_3$] vary. The solutions range from 100% castor oil to a 45/55 blend of toluene and heptane. The test is conducted by applying a drop of test solution to the substrate and waiting 15 s, after which the excess fluid is removed and the area examined for damage. Failure is indicated by darkening of the substrate caused by penetration. The highest numbered solution that stands on the surface without causing failure is reported as the rating.

The second test method used, TAPPI T454, gives an accelerated comparison of the relative rates at which oils or greases may be expected to penetrate papers. The test is done by placing 5 g of sand in a pile on the substrate and saturating the sand with 1.1 mL of colored turpentine solution. The substrate is placed on top of white paper to allow for easy identification of staining beneath the substrate, indicating penetration. The results are reported as the time elapsed from the addition of turpentine to the first sign of paper staining. If staining has not occurred within 30 min, the test is terminated and reported as 1,800+ s.

To assess the performance of the water-resistant paper, water absorption (Cobb tests[4]) and water-vapor transmission rate (WVTR) tests were conducted. WVTR is a measure of the passage of water vapor through a substrate. The WVTR testing was done per ASTM E96.[5] The Cobb test determines the amount of water (g/m^2) absorbed by the substrate within a specified time.

Films

Performance of the VPCI cohesive film is assessed through peel resistance and shelf life stability. Peel resistance is tested per ASTM D1876[6] and determines the relative peel resistance of adhesive bonds between flexible adherends. This test is conducted by cutting 1 by 4 in (25 by 102 mm)-wide test strips, which are bonded end to end in a string. The ends of the film are then attached to an Instron Tensile Tester[†] and the value is recorded when peeling of the cohesive layers is observed. Shelf life determination is conducted per the GM shelf life test[7] for cohesive films. An arbitrary part is sealed within a pouch of the cohesive material so that 3 in (76 mm) of cohesive layer are exposed on all sides. The pouch is then exposed to elevated temperatures and relative humidity for seven days. Any deterioration of the adhered layers is cause for failure.

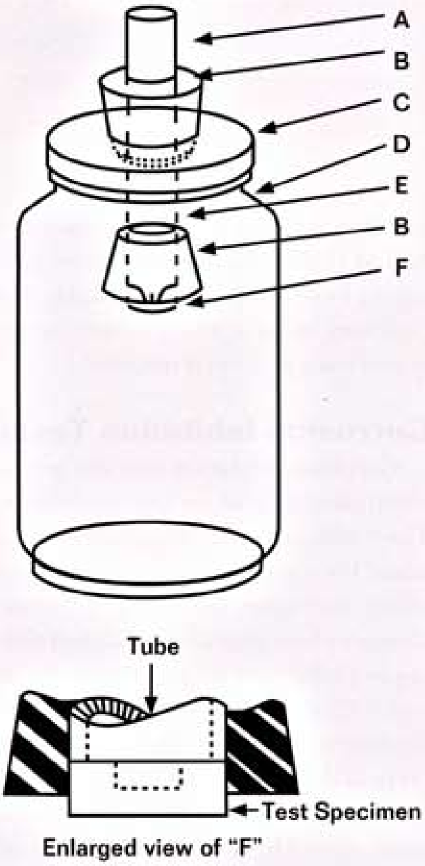
Linerboard

The coefficient of friction (COF) for the anti-skid linerboard was determined per ASTM D1894.[8] This test determines the coefficients of starting and sliding friction of the test substrate over itself as well as other materials such as metal. The test employs a 2.5 by 2.5-in (63 by 63-mm), 200-g sled pulled at a speed of 11.8 in/min (300 mm/min) and the COF is calculated by Equation (1).

$$\text{COF} = \frac{\text{Force to cause sliding of substrate (g force)}}{\text{Sled weight (g force)}} \qquad (1)$$

FIGURE 1

VIA Test Apparatus



Enlarged view of "F"

A **Water retainer**—Aluminum tube 11.4 cm in length, 1.6 cm OD, and 1.3 cm ID. The tube shall have a capacity of 16 mL distilled water at 24 ± 2 °C.

B **Rubber stoppers**—Two no. 6 1.3-cm rubber stoppers with a 1.3-cm hole bored through centers.

C **Jar lids**—Plastic screw-type lid, with 3-cm holes drilled through the center with two 0.6-cm holes 2.5 cm apart near the edge.

D **Jars**—1-L size, mouth size 6 cm diameter, 17.7 cm in height, 13.6 cm ID.

E **Insulating sleeve**—1.3-cm ID rubber tubing, length 3.8 cm.

F **Steel specimen**—1.6-cm OD, 1.3 cm long with 0.9-cm-deep flat bottom hole drilled in center (0.8-cm wall cup).

TABLE 1

Grease-resistant properties

Test Method	Grease-Resistant Paper	Waxed Paper	Polycoated Paper
Test Kit	9	7	9
TAPPI T-454	1,800+ s	<60 s	1,800+ s

The water-resistant paper was evaluated for the amount of water absorbed by a 2-min Cobb test, and for the transmission rate of water vapor (ASTM E96) (Table 2). Results were good.

TABLE 2

Physical properties of water-resistant paper

Test Method	Result
Cobb Test	4.0-5.0 g/m^2
WVTR (73 °F [23 °C], 50% relative humidity)	3.528 g/day·m^2

The coefficient of friction for the anti-skid linerboard was determined according to ASTM D1894 (Table 3). The test was conducted to determine the COF for linerboard on linerboard as well as linerboard on metal and compared to a commercially available anti-skid linerboard.

TABLE 3

Anti-skid linerboard coefficient of friction

Test Method (ASTM D1894)	VPCI Anti-Skid Linerboard	Typical Anti-Skid Linerboard
Linerboard to linerboard	0.454	0.295
Linerboard to metal	0.243	0.201

TABLE 4

Razor blade test results (CS)

Sample	Panel 1	Panel 2	Panel 3
Grease-resistant paper	Pass	Pass	Pass
Water-resistant paper	Pass	Pass	Pass
Anti-skid linerboard	Pass	Pass	Pass
Masking film	Pass	Pass	Pass
Cohesive film	Pass	Pass	Pass
Control	Fail	Fail	Fail

Properties of VPCI masking film include tack, peel adhesion, and unwind force of the roll. The tack is measured according to ASTM D3121.[9] This test apparatus involves a small ramp with a 2 9/16-in (65-mm) incline at a 21 to 30-degree angle and a distance of 7 in (178 mm). A 1-in-diameter, 20-g steel ball is released from the top of the ramp and rolls over the adhesive substrate. The time to travel across a given distance over the substrate is then recorded. Peel adhesion is tested per ASTM D3330[10] and demonstrates the relative bond strength of an adhesive substrate to various surfaces. The test gives a measure of adherence, when peeled at a 180-degree angle, to a standard metal panel. The force required to unwind a roll of pressure-sensitive tape (unwind force) is assessed per ASTM D3811.[11] This test involves pulling the loose end off the roll roughly 6 in (152 mm) using a tensile tester; the required force to do so is recorded.

Corrosion Inhibition Tests

Corrosion inhibition tests are generally applicable to all packaging products. Three different tests are conducted to assess the contact, barrier, and vapor-phase corrosion inhibiting abilities. Contact-phase corrosion inhibition testing is performed by the Razor Blade test.[12] Carbon steel (CS) panels are cleaned in methanol and dried. Two drops of deionized water are placed on a metal panel and covered with the substrate. After 2 h, the substrate is removed and the panels inspected for any sign of corrosion, pitting, or staining. This test can be adapted to other metals such as copper, galvanized steel, or aluminum with a slight modification in the test solution used for each metal (0.005% sodium chloride [NaCl], 3.5% sodium acetate [$NaC_2H_3O_2$], or 3.5% NaCl, respectively) and the exposure time.

Barrier-phase corrosion inhibition is tested per the SO_2 (sulfur dioxide) Test,[13] which evaluates the substrate's performance as a barrier against an aggressive SO_2 environment. The test is made by wrapping CS panels within the substrate and conditioning them in a 1-gal (3.785-L) jar for 20 h at ambient temperature. An SO_2 gas environment is then created within the jar and the wrapped panels are

TABLE 5

Razor blade test results (copper)

Sample	Panel 1	Panel 2	Panel 3
Grease-resistant paper	Pass	Pass	Pass
Control	Fail	Fail	Fail

TABLE 6

SO_2 test results

Sample	Panel 1	Panel 2	Panel 3	Control
Grease- resistant paper	Grade 4	Grade 4	Grade 4	Grade 0
Water-resistant paper	Grade 4	Grade 4	Grade 4	Grade 0
Anti-skid linerboard	Grade 4	Grade 4	Grade 4	Grade 0
Masking film	Grade 4	Grade 4	Grade 4	Grade 0
Cohesive film	Grade 4	Grade 4	Grade 4	Grade 0

TABLE 7

VIA test results

Sample	Plug 1	Plug 2	Plug 3	Control
Grease-resistant paper	Grade 3	Grade 3	Grade 3	Grade 0
Water-resistant paper	Grade 3	Grade 3	Grade 3	Grade 0
Anti-skid linerboard	Grade 3	Grade 3	Grade 3	Grade 0
Masking film	Grade 3	Grade 3	Grade 3	Grade 0
Cohesive film	Grade 3	Grade 3	Grade 3	Grade 0

exposed to this environment in a cycling oven at 50 °C for 16 h, followed by room temperature for 8 h. The jars are then removed from the oven and the panels are unwrapped and visually inspected for corrosion. The panels are graded on a scale of 0 to 4, where 0 is heavily corroded (covering >25% of the panel) and 4 means no visible corrosion on the panel surface.

Vapor-inhibiting ability (VIA)[14] tests the products' ability to protect metals from corrosion without coming into direct contact. CS plugs are sanded in one direction with 120-grit silicon-carbide sandpaper and rinsed in methanol. The plugs are then polished at a 90-degree angle to the initial grind with 320-grit paper, rinsed in methanol, and dried. The test apparatus consists of a 1-L jar with a modified lid (Figure 1). The cleaned plugs are then inserted into the rubber stoppers. Strips of the test substrate (1 by 6 in) are hung from the inside of the lid and not in contact with the plug. The lids are screwed on tightly 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 they are left to sit at ambient temperature for 2 h, followed by 2 h in a 40 °C oven. After this, the plugs are removed and their surfaces inspected for corrosion. The plugs are rated on a scale of 0 to 3, where 0 is heavily corroded (showing no corrosion inhibition), and 3 means no visible corrosion and good inhibiting effects.

Results

Physical Properties

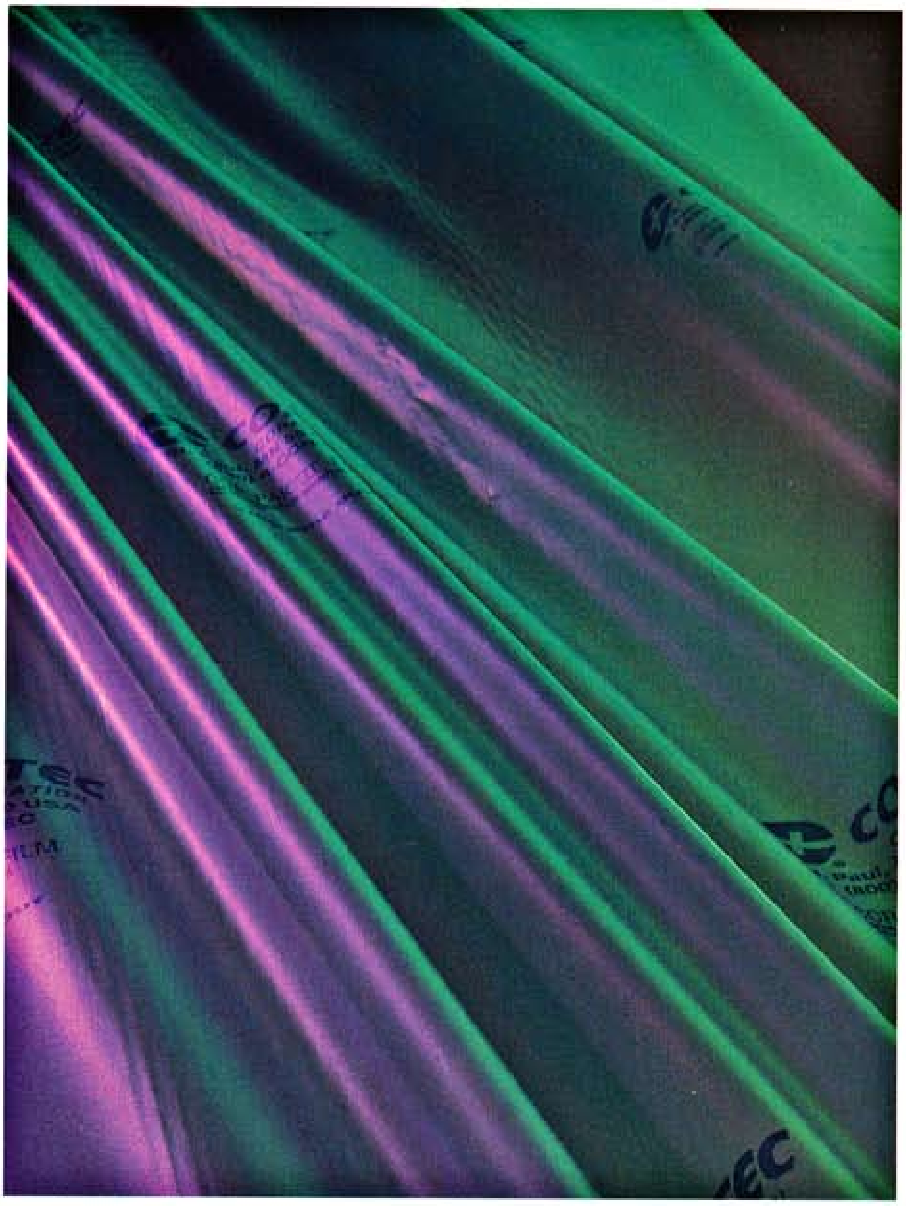
For comparison purposes, the grease-resistant corrosion inhibiting paper was tested alongside polycoated paper and waxed paper (Table 1). The environmentally friendly grease-resistant paper demonstrates an equivalent, or higher, level of performance in comparison to traditional products.

Corrosion Inhibiting Properties

The corrosion inhibiting properties of each product are shown in Tables 4 to 7. Table 4 shows the contact-phase corrosion protection as determined by the Razor Blade test. Table 5 shows the contact-phase protection offered by the grease-resistant paper for non-ferrous metals such as copper. Table 6 shows the barrier-phase corrosion inhibiting ability of the five products discussed. Table 7 shows the vapor-phase corrosion inhibition offered by each product. The controls employed for each of these tests are a non-coated substrate of the same material; for the grease- and water-resistant papers, the control is virgin base stock (40- and 37-lb/3,000 ft², respectively), the anti-skid linerboard control is an untreated 42-lb/1,000 ft² linerboard, and the cohesive and masking films utilize an untreated polyethylene film as the control. The test results verify that each of the VPCI packaging products described above exhibit excellent corrosion inhibiting abilities in all three phases: contact, barrier, and vapor-phase.

Conclusions

Aqueous, non-toxic coating chemistries have permitted expansion in the physical properties of VPCI packaging



products, broadening their application ranges and markets. This approach has created products ranging from grease- and water-resistant corrosion inhibiting papers to VPCI-containing adhesive films and other future possibilities. This "greener" process permits environmentally friendly finished products, and also reduces workplace hazards by removing harmful solvents and chemicals from the coating process. Green coating solutions help relieve our dependence on non-renewable energies, and also reduce our carbon footprint and greenhouse gas emissions. Achieving high-performance properties of water-based and bio-based chemistries has been most difficult to do, but each of the five products discussed have demonstrated the capabilities and potential of green technologies.

References

1 C. Hogue, *Chem. Eng. News* 86, 9 (2008).

2 TAPPI T 454, "Turpentine Test for Voids in Glassline and Greaseproof Papers" (Norcross, GA: TAPPI, 1994).

3 TAPPI T 559, "Grease Resistance Test for Paper and Paperboard; TAPPI UM 557, "Repellency of Paper and Board to Grease, Oil and Waxes (Kit Test)" (Norcross, GA: TAPPI, 2002).

4 TAPPI T 441, "Water Absorptiveness of Sized (Non-Bibulous) Paper, Paperboard, and Corrugated Fiberboard (Cobb Test)" (Norcross, GA: TAPPI, 2004).

5 ASTM E96, "Standard Test Methods for Water Vapor Transmission of Materials" (West Conshohocken, PA: ASTM, 2000).

6 ASTM D1876, "Standard Test Method for Peel Resistance of Adhesives (T-Peel Test)" (West Conshohocken, PA: ASTM, 2001).

7 GM Shelf Life Test, Specification #OA034711 (1985).

8 ASTM D1894, "Standard Test Method for Static and Kinetic Coefficients of Friction of Plastic Film and Sheeting" (West Conshohocken, PA: ASTM, 2006).

9 ASTM D3121, "Standard Test Method for Tack of Pressure Sensitive Adhesive by Rolling Ball (West Conshohocken, PA: ASTM, 2006).

10 ASTM D3330, "Standard Test Method for Peel Adhesion of Pressure Sensitive Tape" (West Conshohocken, PA: ASTM, 2006).

11 ASTM D3811, "Standard Test Method for Unwind Force of Pressure Sensitive Tapes" (West Conshohocken, PA: ASTM, 2006).

12 Razor Blade Test, Cortec Corp. Work Instruction, Version 5 (St. Paul, MN: Cortec Corp., May 2008), pp. 1-3.

13 SO_2 Test, Cortec Corp. Work Instruction, Version 6 (St. Paul, MN: Cortec Corp., May 2008), pp. 1-9.

14 VIA Test, Cortec Corp. Work Instruction, Version 11 (St. Paul, MN: Cortec Corp., August 2008), pp. 1-9.

This article is based on CORROSION 2009 paper no. 09486, presented in Atlanta, Georgia.

Kristy Gillette is a product development technologist at Cortec Corp., 4119 White Bear Pkwy., St. Paul, MN 55110. She has been with the company for 18 months, working on the research and development of new packaging products. She has a B.S. degree in chemistry from the University of Wisconsin-Eau Claire and an M.S. degree in organic chemistry from Indiana.

Bob Berg is a former employee of Cortec Corp.

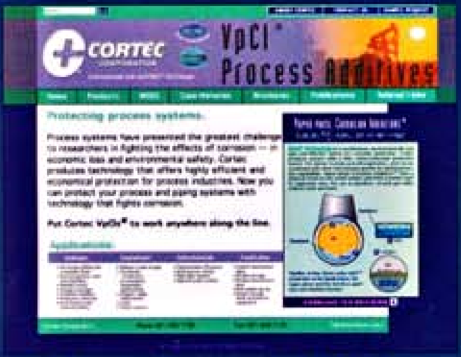
Margarita Kharshan is a laboratory director at Cortec Corp. She has developed and tested corrosion inhibitors for the last 14 years. She has more than 12 patents and has published numerous articles in different magazines. She has a Ph.D. from Moscow Lenin University.

www.CortecVCI.com

www.CortecMothballing.com

www.CortecWaterTreatment.com

www.CortecMetalworking.com



www.CortecProcessAdditives.com

www.CortecMCI.com

www.CortecPackaging.com

www.MilCorr.com