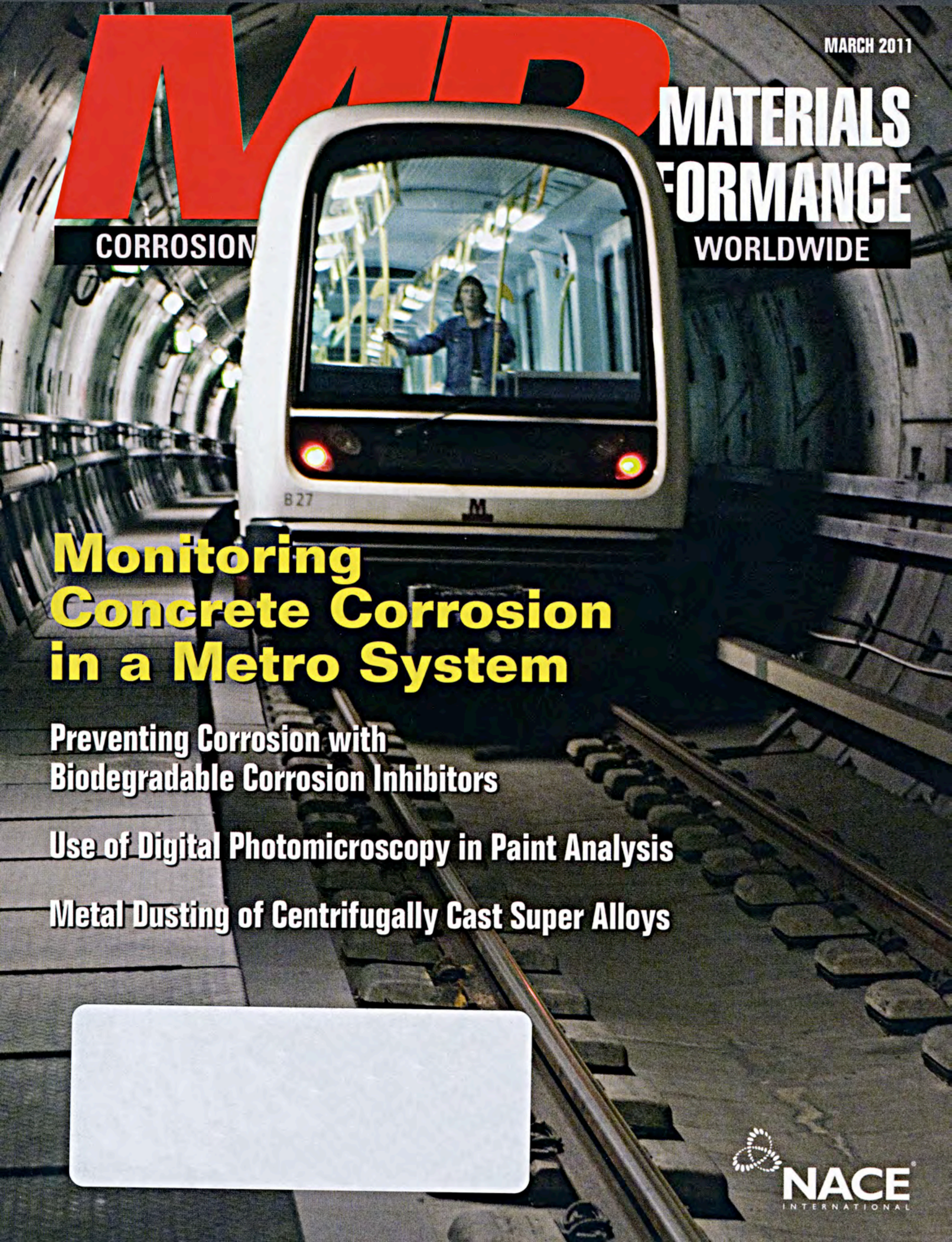
THIS MONTH: CORROSION TESTING, MONITORING, & INSTRUMENTATION

MARCH 2011

MP MATERIALS PERFORMANCE

CORROSION WORLDWIDE



Monitoring Concrete Corrosion in a Metro System

Preventing Corrosion with Biodegradable Corrosion Inhibitors

Use of Digital Photomicroscopy in Paint Analysis

Metal Dusting of Centrifugally Cast Super Alloys

NACE INTERNATIONAL

Applications for Biodegradable Vapor Phase Corrosion Inhibitors

MARGARITA KHARSHAN AND CLIFF CRACAUER,
Cortec Corp., St. Paul, Minnesota

Oil- and solvent-based products have been used for years to protect metal. These products often contain hazardous ingredients and are nondegradable. By incorporating vapor phase corrosion inhibitors in naturally derived solvents such as vegetable oils and their esters, corrosion protection can be obtained with environmentally friendly, biodegradable products. This article describes laboratory tests and industrial applications of these inhibitors.

"Green" chemistry is a dedication to a process for continual improvement, wherein the environment is considered along with the chemistry. Chemical products should be designed to preserve the efficiency of function while reducing their impact on the environment.

The development of green corrosion inhibitors is a process that requires knowledge of pertinent regulations, evaluation of the environmental performance for the environment to which the product will be exposed, and the corrosion protection required in operational applications.

Three approaches can be used to obtain an environmental profile for corrosion inhibitors utilized in a specific application. The most common method is to replace solvent- or oil-based carriers with water-based technology. These technologies provide an environmentally conscious method of corrosion protection,[1] but they can be cost and time prohibitive for certain operations. In these cases, the manufacturer must use environmentally hazardous petroleum-based products or simply do nothing. The second option is to replace petroleum-based carriers with solvents manufactured from environmentally friendly, renewable resources. This has been accomplished by combining vapor corrosion inhibitors (VCIs) with soy-derived and canola oils to formulate anticorrosion products for many applications. The last method is to utilize biodegradable materials as corrosion inhibitors, and conventional solvents as carriers.

This article will be limited to the last two approaches. The goal is to show that, depending on the system, nontoxic products may inhibit corrosion as well or better than their more toxic traditional counterparts.

The products in this article will be represented as:

- VCI A—Soya methyl ester-based cutting fluid

- VCI B—Soya methyl ester-based all-purpose lubricant
- VCI C—Canola oil-based temporary coating for inside or sheltered metal protection
- VCI D—Canola oil-based open atmosphere rust preventive

Development

In developing the green products, a battery of testing was undertaken to ensure that desired properties were achieved. These included physical properties, corrosion-inhibiting properties, and additional functional properties. The physical properties were established by using corresponding petroleum-based products as a baseline. Corrosion-inhibiting capabilities were established using industry-accepted testing. Additional functional properties were evaluated based on the similarity with petroleum-based counterparts whenever possible.

An assortment of standard tests was used to compare the new VCI products with products that are commercially available. Testing included a humidity test, immersion test, cast-iron chip test, salt spray chamber test, vapor inhibiting ability (VIA) test, and other tests to demonstrate the combination of the properties. Marine toxicity, biodegradability, and bio-based content of the tested products were evaluated.

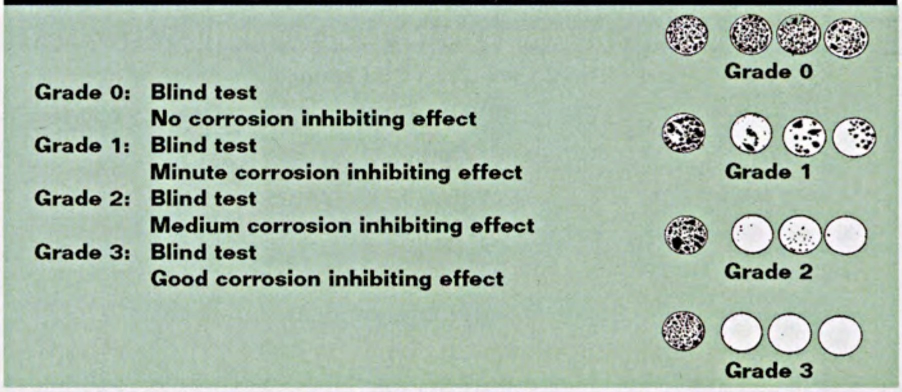
The ASTM D1748-83[2] test method was used to determine rust-preventive properties of metal preservatives under high humidity. Metal specimens were treated with a rust-preventive and then were exposed to temperatures of 48.9 °C ± 1.1 °C (120 °F ± 2 °F) and 95% relative humidity for a given time period. Testing was done for comparative analysis and the time period was dependent on the failure mechanism.

Using DIN EN ISO 6270-2,[3] metal specimens were treated with rust preventive and exposed to temperatures of 40 °C ± 2 °C (104 °F ± 3 °F) and 100% humidity for 168 h (7 days). The test was performed by the University of Zagreb in Croatia.

The ASTM B117[4] test method was conducted to determine rust-preventive properties of a metal preservative in salt spray conditions. Metal specimens treated with the rust preventive were subjected to 35 ± 1.1 to 1.7 °C (95 ± 2 to 3 °F) and 5% sodium chloride (NaCl) concentration in the air.

Using the ASTM G31-72[5] half immersion and Mil-PRF-16173E[6] immersion corrosion tests, carbon steel (CS) panels were weighed and immersed in

FIGURE 1



VIA test grades.[7]

TABLE 1

Preventive properties of metal preservatives under high humidity

ASTM D1748-83 on 1010 CS		
Sample	**Time Before Corrosion (h)**	
VCI A	200	
VCI B	300	
VCI C	>500	
VCI D	7,000	
DIN EN ISO 6270-2		
Sample (5%)	**Results after 168 h**	
VCI A	No corrosion	
Conventional semi-synthetic cutting fluid	Heavy corrosion	
Conventional soluble oil cutting fluid	Corrosion	
ASTM D1748-83 on Heat-Treated CS Gears		
Sample	**Dilution**	**Hours to Failure**
VCI A	5% in water	>108
VCI synthetic water soluble fluid	5% in water	108
Soluble oil cutting fluid	6% in water	<13.5
Control (no coating)	—	<13.5

TABLE 2

Performance of CS bearings under high humidity

ASTM D1748-83 on CS Bearings		
Sample	**Dilution**	**Hours to Failure**
VCI C	Undiluted	>120
VCI water-soluble Rust preventive	10% in water	120
VCI petroleum Rust preventive	33% in naphthenic	>120
VCI petroleum Rust preventive	10% in naphthenic	>120
Commercial rust Preventative	Undiluted	120

TABLE 3

Preventive properties of metal preservatives under salt spray and immersion conditions

ASTM B117 on 1010 CS	
Sample	**Hours of protection**
VCI D	500+
Conventional open-atmosphere rust preventive	168

ASTM G31-72 Half Immersion Corrosion		
Alloy	**Time Before Corrosion (Days) Control**	**Time Before Corrosion (Days) VCI C**
3041 Bare Al	<1	>30
1010 CS	<1	>30

MIL-PRF-16173E Immersion Corrosion Testing (VCI D)			
Specimens	**Requirements (Weight Loss in mg/cm²)**	**Results (Weight Loss in mg/cm²)**	**Pass/Fail**
Brass	<1.0	0	Pass
Zinc	<7.5	0.4	Pass
Magnesium	<0.5	0	Pass
Aluminum	<0.2	0.05	Pass
Steel	<0.2	0	Pass
Lead-calcium	<5.0	0	Pass

the test solution, with deionized (DI) water as a control solution. The testing period was determined by the alloy used. The panels were removed after the predetermined testing period, cleaned, and tested for weight loss. Immersion tests were done on different metals in accordance to Mil-PRF-16173E (2, 3). According to this test, the specimen is immersed in the solution for one week at 55 °C (131 °F).

The ASTM D4627-86[8] method was used to evaluate the ferrous corrosion control characteristics of water-soluble metalworking fluids. In this test, Class 30 gray cast iron chips were submersed in various dilutions of a water-soluble (or emulsified) fluid to determine the minimum dilution that affords corrosion protection. A ladder study was used to determine the lowest concentration that would pass the testing requirements.

A VIA test was performed according to Federal Test Method Standard No. 101C.[9] One gram of the inhibitor was introduced into a quart jar with a highly polished CS specimen inside. The jar was sealed with the lid. After conditioning at room temperature for 2 h, a 3% solution of glycerin in DI water was added. The sealed jar was placed into the oven at 40 °C for 2 h. After exposure, the condition of the metal specimen was visually inspected and rated according to the guidelines in Figure 1.[7]

The biodegradability was determined in accordance with the EPA 28-day test method.[10] The requirement states that the ratio of biological oxygen demand (BOD) to chemical oxygen demand (COD) must be greater than or equal to 60%.

Bio-based content is the percentage of the total carbon that is modern (present day) in origin. Analyses were performed using conventional radiocarbon analytical methods. These tests were performed by Iowa State University.

The ASTM D4172[11] lubricity test is a four ball wear test. ASTM D2670[12] was used for VCI A. Tests were performed by Petro-Lubricant Testing Laboratories, Inc.

For the floating coating test, water-insoluble product (0.3%) was added to salt water (3.5% NaCl). The steel panel was immersed in the solution. Film-forming properties of oil-based product were evaluated by changing the water a few times and visually observing the panel.

Results

In the formulation of VCI A and VCI B, soybean oil methyl ester was used as a

TABLE 4

Cast iron chip and lubricity testing results

	ASTM D4627-86 (Cast Iron Chip Test[A])		
Percent of Soy-Derived Cutting Fluid (in Water)	Sample 2	Sample 3	Sample 4
5	No corrosion	No corrosion	No corrosion
4	No corrosion	No corrosion	No corrosion
2.5	No corrosion	No corrosion	No corrosion
1	No corrosion	No corrosion	No corrosion
0.5	5% corrosion	5% corrosion	5% corrosion
0.1	80% corrosion	80% corrosion	80% corrosion

[A] Conventional soluble oil cutting fluid passes this test in concentrations from 5 to 2.5% only

	VIA Test Results		
Sample	Plug #1	Plug #2	Plug #3
VCI C	Grade 3	Grade 3	Grade 3
VCI D	Grade 3	Grade 3	Grade 2

	ASTM D4172 Lubricity Testing	
Sample	Conditions	Results (Scar Diameter)
VCI B	40 kg, 1,200 rpm, 1 h at 75°C	0.30 mm
Conventional lubricant	Same	0.87 mm

carrier to give high solvency and additional lubricating properties.

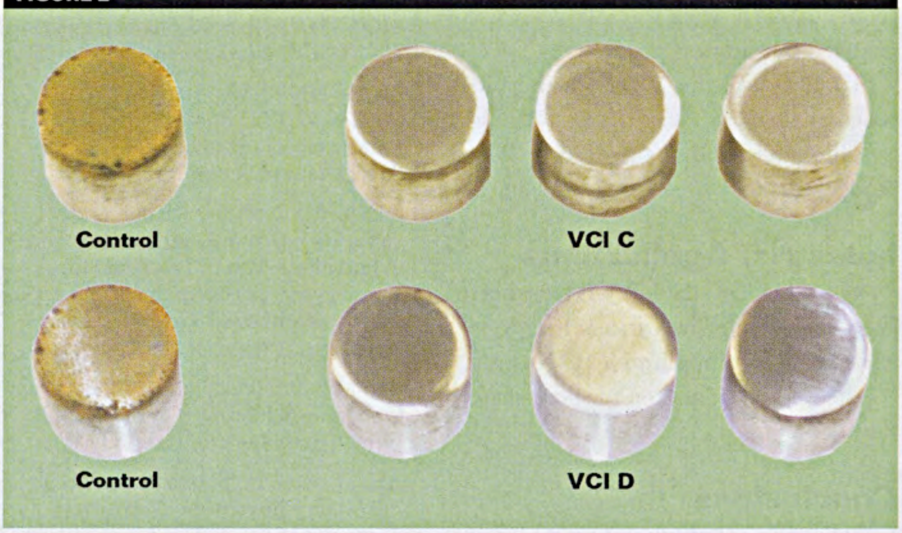
VCI C and VCI D were formulated with canola oil as a carrier because canola oil contains less saturated fatty acids, adds corrosion protection, and doesn't attack coated surfaces. It can be applied on top of coated metals and has a low freezing point (–20 °C [–4 °F]), allowing application in low temperatures.

Results of the humidity test varied from one test to another depending on three factors: the metal substrate, the specific VCI, and dilution in water that was used. All were factors in the length of time before failure. In each case, the VCI products outperformed the conventional water-based and petroleum-based products. They also performed equally to or better than other water-based and petroleum-based VCI products. Tables 1 and 2 show the results.

Salt spray testing was performed on VCI D, an open atmosphere corrosion inhibitor. Table 3 presents the results.

The control panels in the half-immersion test show medium corrosion below the water line after 24 h for CS, and corrosion above the water line after 72 h. The aluminum controls have oxidation below the aqueous line after 72 h. In the same test, the VCI showed no corrosion for >30 days, indicating the product has both contact and vapor-protection capabilities. Table 3 shows the results of the half immersion testing. In the immersion corrosion test, VCI D outperformed all requirements of military test MIL-PRF-16173E (Table 3).

FIGURE 2



Results of the VIA test.

The VCI soy-derived cutting fluid passed the cast iron chip test at a lower concentration than the standard water-soluble and VCI water-soluble cutting fluids (Table 4).

The VIA test was performed for VCI C and VCI D. The results are compared to conventional open-atmosphere rust preventive (Table 4 and Figure 2).

Lubricity testing was performed for VCI A and VCI B, which are used as machining fluids. Tables 4 and 5 present the results.

TABLE 5

Lubricity testing results

	ASTM D2670 Lubricity Testing	
Sample	**Conditions**	**Results**
VCI A	Run in 5 min—159 kg, gauge load—408 kg	Total teeth wear 17 (2.5% solution) 10 (5% solution) Seizure (yes/no) 2.5% solution—no 5% solution—no
	Bio-based content (modern carbon)	
Sample	**%C14**	
VCI A	67% (experimental)	
VCI B	91% (experimental)	
VCI C	95% (theoretical)	
VCI D	65% (theoretical)	

VCI C showed very good performance in the floating coating test. It formed a very persistent film on the metal surface. This film provided protection to the metal even when the salt water was changed five times.

Table 5 lists the results of the bio-based analyses.

All tested products are 70 to 98% biodegradable.

Industrial Applications

These biodegradable VCIs have been used successfully in various locations. Most notable are applications in Norway, Sweden, Europe, and on offshore structures.

Conclusions

Following extensive testing and field trials, it is apparent that VCI bio-based products will be a viable and important method for interim corrosion prevention now and in the future. These products exhibit excellent corrosion inhibiting properties both in laboratory and real-world environments. Also, most of these products demonstrate additional functional features. Since they are biodegradable and produced from a renewable resource, they will continue to gain market acceptance as environmentally conscious products become preferred.

References

1 C. Cracauer, M. Kharshan, "Interim Corrosion Protection With Soy-Based Products Incorporating Vapor Phase Corrosion Inhibitors," CORROSION 2003, paper no. 03485 (Houston, TX: NACE International, 2003), p. 58.

2 ASTM D1748-83, "Standard Test Method for Rust Protection by Metal Preservatives in the Humidity Cabinet" (West Conshohocken, PA: ASTM).

3 DIN EN ISO 6270-2, "Paints and varnishes—Determination of resistance to humidity—Part 2: Procedure for exposing test specimens in condensation-water atmospheres" (Geneva, Switzerland: ISO).

4 ASTM B-117-85, "Standard Practice for Operating Salt Spray (Fog) Testing" (West Conshohocken, PA: ASTM).

5 ASTM G31-72, "Standard Practice for Laboratory Immersion Corrosion Testing of Metals" (West Conshohocken, PA: ASTM).

6 Mil-PRF-16173E, "Corrosion Preventative Compound, Solvent Cutback, Cold Application" (Washington, DC: MIL).

7 Modified Figure 12 from NACE Standard TM0208-2008.

8 ASTM D4627-86, "Standard Test Method for Iron Chip Corrosion for Water-Dilutable Metalworking Fluids" (West Conshohocken, PA: ASTM).

9 FED-STD-101C (Notice 4), "Federal Standard: Test Procedures For Packaging Materials" (Washington, DC: FED, 2002), S/S BY MIL-STD-3010.

10 EPA Biodegradability Test Method (BOD, COD), 28 days.

11 ASTM D4172, "Standard Test Method for Wear Preventative Characteristics of Lubricating Fluids (Four-Ball Method)" (West Conshohocken, PA: ASTM).

12 ASTM D2670, "Standard Test Method for Measuring Wear Properties of Fluid Lubricants (Falex Pin and Vee Block Method)" (West Conshohocken, PA: ASTM).

This article is based on CORROSION 2010 paper no. 10147, presented in San Antonio, Texas.

MARGARITA KHARSHAN is the laboratory director at Cortec Corp., 4119 White Bear Pkwy., St. Paul, MN 55110, e-mail: rkharshan@cortecvci.com. She has 18 years of experience developing and testing corrosion inhibitors, holds more than 15 patents, and has published numerous papers. She has a Ph.D. from Moscow Lenin University.

CLIFF CRACAUER is vice president of Sales at Cortec Corp., e-mail: cliff@cortecvci.com. He has 12 years of experience at the company and previously held the positions of technical service engineer and technical sales manager. He has a B.S. degree in chemistry from the University of Minnesota's Institute of Technology, holds two patents, and has published seven papers. He is a five-year member of NACE International. MP