Slow Release Corrosion Inhibiting Block

Boris Miksic, FNACE, Margarita Kharshan, Ming Shen, and Alla Furman, *Cortec Corp., St. Paul, Minnesota*
Ali Bayane, *Bionetix International, Montreal, Quebec, Canada*

A corrosion inhibitor releasing block is formulated using renewable soybean-based wax and proven vapor phase corrosion inhibitor technology. A bench test and pilot cooling tower test show that when immersed in water, the inhibitor releasing block slowly dissolves and releases a calculated amount of inhibitors. The inhibitors provide corrosion protection to multimetals and can be used as a corrosion inhibitor additive in most water treatment programs. It is also compatible with the majority of commercially available biocides and antiscalants.

Water treatment systems are ideal environments for a destructive attack on metals to occur. Slow-release corrosion inhibiting products provide an easy way to combat corrosion in water treatment systems and avoid expensive repairs and disruptions.

Products that slowly release their active ingredients are employed by many industries. Generally a slow-release product incorporates relatively large amounts of active ingredients with an appropriate delivery system to provide a steady concentration of the active components over a specified period of time.

This study includes:

- Selecting the corrosion inhibitor
- Selecting a biodegradable inactive carrier that is based on a renewable source
- Evaluating the compatibility of the inhibitor and the carrier
- Determining the weight ratio of the inhibitor/carrier and the size of the block
- Adjusting the manufacturing technology
- Evaluating the product in a bench test
- Evaluating the product in a pilot cooling tower

Experimental Work

Corrosion Inhibitor Selection

The corrosion inhibitor selected as the active ingredient for the corrosion inhibitor releasing block is the Cortec Building Block†. This inhibitor is a blend of contact and vapor corrosion inhibitors and alkalinity builders. Previous studies and field experience[1] show that it provides effective protection in water treatment at low dosage levels (starting dosage is 7 ppm) when continuously added to makeup water. In addition, the selected inhibitor is very low in toxicity. Table 1(a) contains results from the testing lab.[2]

The results show that the selected inhibitor has a very low impact on the fresh water aquatic life, and the discharge of the inhibitor would not be a concern for environment regulations.

All these data make the selected inhibitor an ideal candidate as the active ingredients in a slow-release format. The inhibitor releasing block provides easy application of a field-proven inhibitor for water treatment protection.

†Trade name.

TABLE 1. TEST DATA

(a) Acute 48-h Static-Renewal Toxicity Test on the Selected Inhibitor		
Sample	**NOEC/LOEC[A] (ppm) D.pulex**	**NOEC/LOEC (ppm) P.promelas**
Test #E-17766-01	10,000/>10,000	10,000/>10,000
[A]NOEC—no observable effect concentration; LOEC—lowest observable effect concentration		

(b) Vapor Inhibition Ability of Inhibitor Releasing Block			
Sample	**Plug 1**	**Plug 2**	**Plug 3**
10 g inhibitor releasing block	3	3	3
Control	0	—	—

(c) Results in Stagnant Water Test (10 Days)		
Medium	**Molybdate Concentration/Corrosion Inhibitor Concentration (ppm)**	**Time Before Corrosion Starts**
Tap water with inhibitor releasing block	90/4,300	>90 days
Tap water only	<0.1	<2 h

(d) Comparison of Corrosion Protection Provided by Inhibitor Releasing Block vs. Similar Amount of the Selected Inhibitor (70 °C for 72 h)[B]				
Sample	**Initial Weight (g)**	**Final Weight (g)**	**Weight Loss (g)**	**Z (% of Protection)**
Control (tap water with 1,200 ppm of $CaCO_3$)	24.7601	24.4162	0.0401	—
0.28% selected inhibitor	22.7601	22.7612	–0.0011	97.2
0.7% inhibitor releasing block	23.1848	23.1871	–0.0023	94.3
[B]1,200 ppm $CaCO_3$ in water				

Inactive Carrier Selection

Several samples of slow release carriers were prepared and evaluated. For the preliminary evaluation, a blend of sodium sulfonates and cocoamides was used as the carrier for the corrosion inhibitor, and the blocks were manufactured by extrusion. Laboratory and pilot cooling tower tests confirmed that the selected corrosion inhibitors can be incorporated in, and later released from, the blocks. Tests in the pilot cooling tower, however, showed that such a carrier was very foamy and dissolved faster than the desired rate for a slow release product.

In the second round of tests, soybean-based waxes were utilized as a carrier. In addition to being biobased and biodegradable, soybean-based waxes were chosen because of their melting points and their tendency to form a microemulsion with water in the presence of specific surfactants. Those waxes, together with sufficient nonionic surfactants and amide-based lubricating components, constitute the inactive carrier of the inhibitor releasing block. The inhibitor releasing block was molded.

Evaluating Inhibitor Releasing Block Performance

The inhibitor releasing block was evaluated in stagnant water conditions in a bench test, and in fast-flowing water conditions in a pilot open recirculating cooling water system. Vapor phase protection of the inhibitor releasing block was evaluated using the vapor inhibiting ability (VIA) test.

The main objectives of evaluating the block in stagnant condition were to determine:

- Average time for complete dissolution of the inhibitor releasing block
- Effect of the inhibitor releasing block on biogrowth
- Effectiveness of the corrosion inhibitors released from the inhibitor releasing block vs. the selected inhibitor

The main objectives of evaluating in the open recirculating cooling tower were to determine:

- The lifespan of an inhibitor releasing block in open recirculating cooling tower
- Its impact on biogrowth
- Its effectiveness in preventing corrosion

Instruments and Materials Used

A carbon steel (CS) coupon (SAE1010) (UNS G10100) was used in stagnant water testing and in pilot cooling tower testing. A galvanized steel coupon (hot-dip, ASTM A525-93[3]), and a copper coupon (CA110, QQ-C576) (UNS C11000) were used in the pilot cooling tower testing. Corrosion rate was determined by coupon weight loss. Coupons were cleaned with laboratory-grade methanol prior to testing. Corrosion products after testing were removed according to the cleaning procedure of ASTM G1-03 (2011).[4]

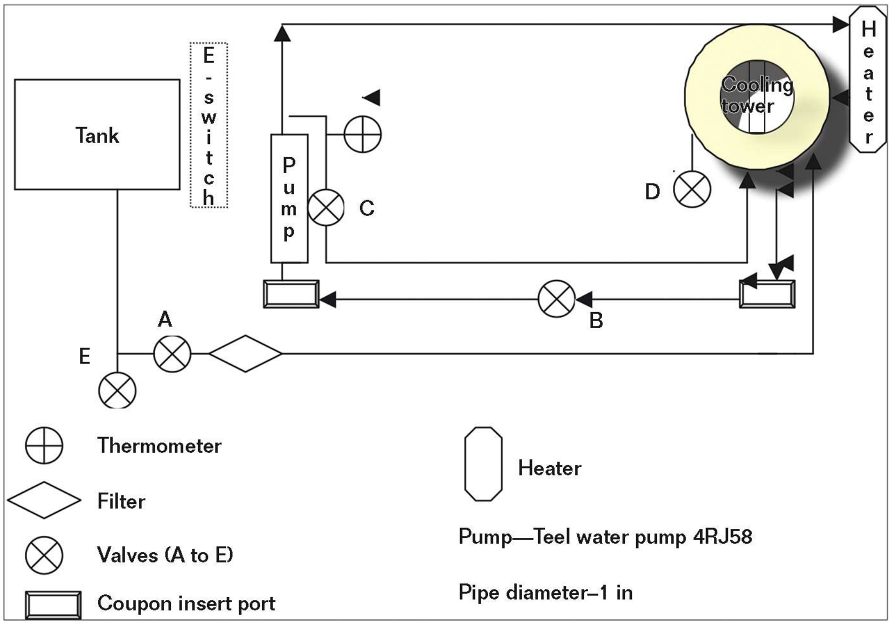


FIGURE 1 Open recirculating cooling tower flow chart.

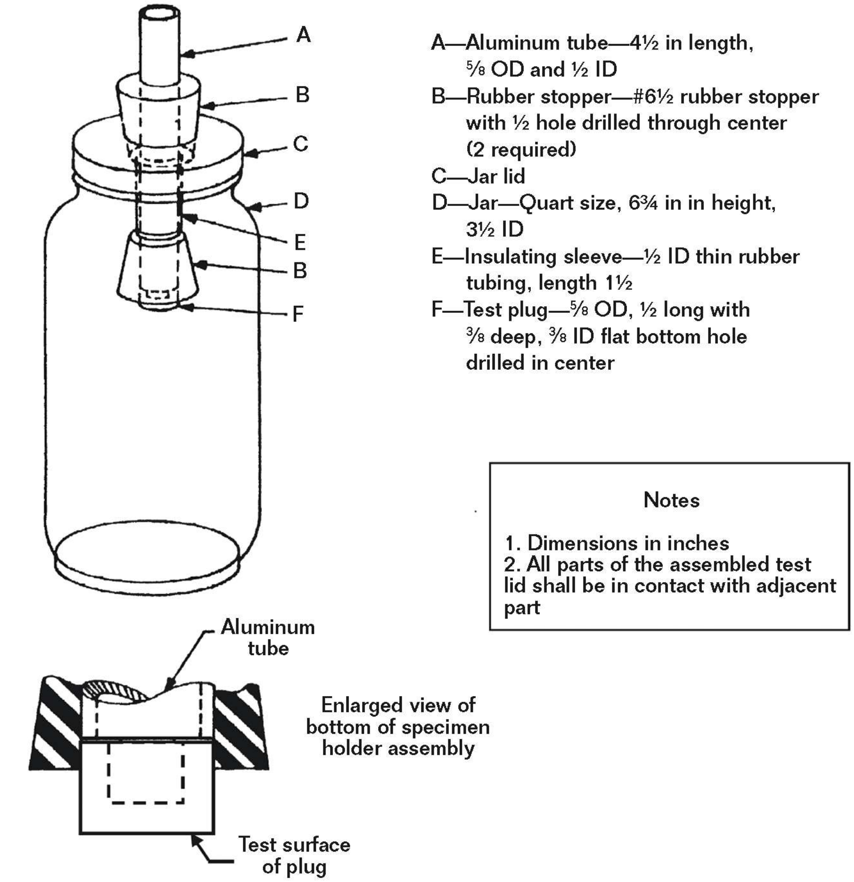


FIGURE 2 Illustration of the VIA test assembly.

Instruments included the following:

- An MO-2 molybdate test kit (Hach†) to measure the amount of a molybdenum-based tracer to determine the inhibitor concentration released from the inhibitor releasing block
- A total dissolved solids (TDS) meter (OAKTON EC/TDA/Salt Testr†)
- A pH meter (IQ Scientific Instruments†)
- BTM-2 Duo Bio Dipslides (WET International, Inc.†) to check bio growth in water
- The pilot cooling tower (RSD–005†) has a ½-hp pump and a flow rate of ~30 gpm (114 L/min). Water velocity inside the circulating pipe was ~298 m/min (Figure 1)
- A VIA test kit (see Test Procedures, Evaluating Vapor Inhibiting Ability).

Test Procedures

Evaluating Vapor Inhibiting Ability

The VIA test evaluates a product's ability to protect metal from corrosion without being in direct contact with it. The method used is based on MIL-STD-3010B,[5] Method 4031. Figure 2 shows an illustration of the VIA test assembly. A sample of the inhibitor releasing block material was placed in a dish inside a capped quart-sized jar with a freshly polished and cleaned CS plug (SAE 1010) for 20 h at ambient temperature. A relative humidity of ~100% was then created in the jar (via the addition of 3% glycerol in water) for 2 h at ambient temperature, followed by another 2 h at 40 °C. After being removed from the oven, the plugs were inspected and rated on a scale of 0 to 3, where 0 is heavily corroded (no corrosion inhibition), and 3 means no visible corrosion and good inhibiting effects (Figure 3). The test was run in triplicate. The control was a plug exposed in a jar without an inhibitor.

Test in Stagnant Conditions

An inhibitor releasing block was weighed and immersed in 1 L of tap water. After 10 days, the concentration of inhibitor was determined using the molybdate test kit; a CS immersion test was set up in this water. The time lapsed before the

†Trade name.

inhibitor releasing block dissolved (fell apart) was recorded. A solution of 1,200 ppm calcium carbonate ($CaCO_3$) in water was made and used as a blank. Solutions of 0.7% inhibitor releasing block and 0.28% selected inhibitor in the $CaCO_3$ water were made. Immersion of CS was carried out again in the above three solutions.

Test in Pilot Cooling Tower

An inhibitor releasing block was weighed and placed in a basin of the cooling tower. The following steps were taken:

- pH, TDS, and the inhibitor concentration in the circulating water were monitored daily. pH and TDS of the makeup water (tap) also were measured.
- Based on a control run (without the inhibitor releasing block in the tower basin), the blowdown schedule was set at every seven days using the measured cycle of concentration data (within the range of 4 to 6). Bacterial count and weight of the inhibitor releasing block were measured at each blowdown.
- Corrosion tests were performed by inserting coupons of galvanized steel, steel, and copper into the circulating pipe to study the corrosion protection during the lifespan of an inhibitor releasing block. The control was circulating water from a cooling tower operated without inhibitor releasing blocks.

Corrosion rate was calculated using Equation (1):

$$\text{Corrosion rate (mpy)} = (3.45 \times 10^6 \times W)/(A \times T \times D) \qquad (1)$$

where T = time exposure in hours to the nearest 0.1 h, A = surface area of the coupon in cm^2 to the nearest 0.1 cm^2, W = mass change in g, to the nearest 1 mg, and D = density of metal in g/cm^3 (steel = 7.85 g/cm^3; copper = 8.94 g/cm^3).

Percent of corrosion protection was calcuted using Equation (2):

$$\text{Corrosion protection (\%)} \quad Z = \frac{(C_c - C_i)}{C_c} \times 100 \qquad (2)$$

Grade 0: Blind test
No corrosion inhibiting effect
Grade 1: Blind test
Minute corrosion inhibiting effect
Grade 2: Blind test
Medium corrosion inhibiting effect
Grade 3: Blind test
Good corrosion inhibiting effect

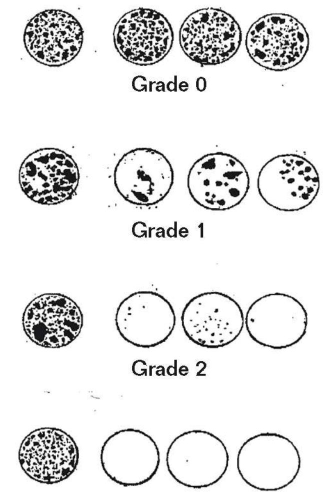
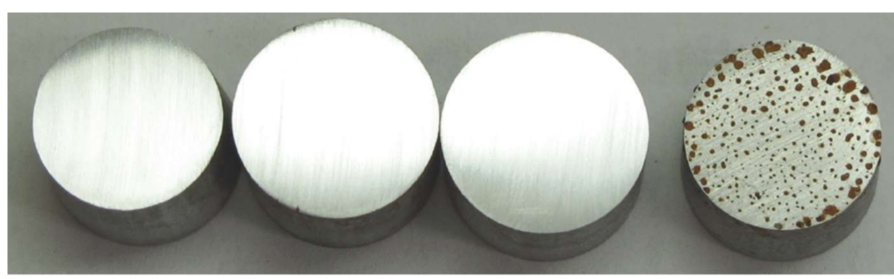


FIGURE 3 The VIA test grading chart (Grade 2 or 3 are passing).



Plug 1 Plug 2 Plug 3 Control

FIGURE 4 CS plug after the VIA test with the inhibitor releasing block.

where: C_c = the corrosion rate without inhibitor and C_i = corrosion rate with inhibitor.

Results

Vapor Inhibiting Ability Test

The inhibitor releasing block showed protection in vapor phase in the VIA test (Table 1[b] and Figure 4).

Tests in Stagnant Water (Bench Results)

It took ~4 months for one inhibitor releasing block to be mostly dissolved in 1 L of stagnant tap water (several small pieces remained). After an inhibitor releasing block had been immersed in 1 L of tap water for 10 days, the concentration of the corrosion inhibitor was found to be 4,300 ppm.

The CS coupon showed no signs of corrosion for 90 days when immersed in the tap water containing the inhibitor releasing block. The control (in tap water) showed signs of corrosion within 2 h (Table 1[c]). Corrosion protection provided by the inhibitor releasing block vs. the selected inhibitor was evaluated by immersing coupons in solutions containing elevated calcium ion content to simulate the conditions of cooling tower operation (Table 1[d]). It showed that the process of incorporating the selected inhibitor into the inhibitor releasing block did not affect the protection effectiveness. The data also suggest that the carrier materials did not provide extra protection.

Test in Pilot Open Recirculating Cooling Tower

The test results show that the inhibitor releasing block dissolved in an even and

TABLE 2. PROTECTION BY INHIBITOR RELEASING BLOCK IN CIRCULATING WATER IN PILOT COOLING TOWER TESTING

	Galvanized Steel	
Condition	**Corrosion Rate (mpy)**	**Z (%)**
Inhibitor releasing block in cooling tower basin	3.06	70.6
Control (no inhibitor)	10.41	—

TABLE 3. BIOGROWTH IN CIRCULATING WATER

	Days of Operation	Bio Dipslide Test
Circulating water without the inhibitor releasing block	5th	10^5 CFU[A]/mL, moderate growth
	12th	10^4 CFU/mL, slight growth
	19th	10^4 CFU/mL, slight growth
Circulating water with the inhibitor releasing block	6.5th	10^3 CFU/mL, very slight growth
	14.5th	10^3 CFU/mL, very slight growth
	20.5th	10^3 CFU/mL, very slight growth

[A]CFU = colony-forming unit

linear fashion. They also show that pH in the circulating water was not affected by the inhibitor releasing block, while the TDS increased when the inhibitor releasing block was added to the cooling tower basin, as expected. Furthermore, the inhibitor releasing block released inhibitor slowly into the circulating water. During the lifespan of an inhibitor releasing block in one pilot test, the inhibitor concentrations in the circulating water were in the range of 150 to 440 ppm.

The circulating water treated with the inhibitor releasing block provided 70% protection for galvanized steel (Table 2). It also provided 45% protection for CS and 6.38% protection for copper. In addition, it slightly reduced biogrowth (Table 3).

Conclusions

Bench Test Data

- The inhibitor releasing block protected in the vapor phase.
- The inhibitor releasing block released corrosion inhibitors from the carrier.
- The steel panel was corrosion-free after 90+ days in the inhibitor releasing block-treated water.
- The immersion corrosion test showed that the manufacturing process of the inhibitor releasing block did not affect the protection effectiveness of the corrosion inhibitors.

Pilot Cooling Tower Experiments

- The inhibitor releasing block dissolved slowly and evenly in a linear fashion. The lifespan of an inhibitor releasing block was about five weeks in a cooling tower basin. To maintain an effective inhibitor concentration level, the useful life of an inhibitor releasing block is probably four weeks.
- The inhibitor releasing block released corrosion inhibitor.
- One inhibitor releasing block treated ~4,200 L (1,904 gal) of water.
- The inhibitor releasing block provided good protection to carbon and galvanized steel.
- The inhibitor releasing block doesn't promote biogrowth in a cooling tower.
- The inhibitor releasing block can be easily placed in make-up water, cooling tower basins, return water circuits, or wastewater systems to provide time-released corrosion inhibitors.

References

1 J. Holden. A. Hansen, A. Furman, M. Kharshan, E. Austin, "Vapor Corrosion Inhibitors in Hydro-Testing and Long Term Storage Application," CORROSION 2010, paper no. 10405 (Houston, TX: NACE International, 2010).

2 "48-Hour Static-Renewal Daphnia Pulex and Pimephales Promelas Toxicity Test Results," Environmental Enterprises USA, 2001.

3 ASTM A525-93, "Specification for General Requirements for Steel Sheet, Zinc-Coated (Galvanized) by the Hot-Dip Process" (West Conshohocken, PA: ASTM International).

4 ASTM G1-03 (2011), "Standard Practice for Preparing, Cleaning and Evaluating Corrosion Test Specimens" (West Conshohocken, PA: ASTM International, 2011).

5 MIL-STD-3010B, "DoD Test Method Standard: Test Procedures for Packaging Material" (Washington, DC: MIL, 2008).

BORIS 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 36 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 40 years.

MARGARITA KHARSHAN is vice president, Research & Development at Cortec Corp., e-mail: rkharshan@cortecvci.com. She has 20 years of experience developing and testing corrosion inhibitors. She holds more than 15 patents and has authored numerous articles in industry journals, including *Materials Performance*. She has a Ph.D. in chemistry from Moscow Lenin University and is a member of the American Chemical Society.

MING SHEN is a research & development engineer at Cortec Corp. Shen has worked for the company for four years, conducting research and development on corrosion inhibitors in water treatment, concrete reinforcement protection, and gas line protection, and has a Ph.D. in chemical engineering from the University of Virginia.

ALLA FURMAN is a senior corrosion engineer at Cortec Corp. She works primarily in the area of formulating and testing corrosion preventive products using various corrosion and electrochemical techniques. The products include water treatment, process additives, metalworking, and concrete admixtures. She has a Ph.D. in engineering.

ALI BAYANE is the quality control and research & development manager at Bionetix International, a subsidiary of Cortec Corp., 21040 Daoust, St.-Anne-de-Bellevue, Montreal, Quebec H9X 4C7, Canada, e-mail: abayane@bionetix.ca. He has seven years of work experience focused on biological treatment of environmental contaminants. He joined Bionetix three years ago and is responsible for research and development in the formation of renewable products for environmental treatment. He has a Ph.D. in applied microbiology and is a postdoctoral of the National Research Council of Canada. MP