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Use of Vapor Phase Corrosion Inhibitors for Galvanized Steel Protection

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A special water treatment program is required for the corrosion protection of galvanized steel in cooling water systems. This article shows the effectiveness and advantage of vapor phase corrosion inhibitors in the protection of different metals, including galvanized steel. The product is biodegradable and has low aquatic toxicity.

Galvanizing is widely used in cooling systems for its ability to protect steel from corrosion and for its cost-effectiveness. This material can offer 20 years or more life expectancy when maintained properly. However, especially when pH is >8.2, corrosion may begin and "white rust" is seen. This oxidized zinc is no longer protecting the steel and the lifespan of the metal system is therefore significantly reduced.[1]

Vapor phase corrosion inhibitors (VpCIs) are available as biodegradable and low-toxicity products that can be incorporated into conventional water treatment programs to provide effective corrosion protection to different metals. This article discusses the performance of a VpCI additive to inhibit corrosion of galvanized steel using various methods, including electrochemical, immersion, and pilot cooling tower tests. Toxicity data are also presented.

Evaluation of Corrosion Protection VpCI Additive to Galvanized Steel

The studied VpCI additive is a synergistic blend of salts of carboxylic acids and alkalinity builders. It can be used alone for corrosion protection or added to existing formulations for a complete water treatment solution. To show protection capabilities, a variety of tests were performed, first on the VpCI alone and then in existing water treatment formulations to obtain corrosion rates from Tafel plots, linear polarization, and weight loss in both bench and cooling tower tests.

Polarization Tests

Tafel plots[2] were obtained using a potentiostat/galvanostat/Versastat[†] with corrosion software model 352/252 SoftCorr[†]. The working electrode was Z15001 zinc, the counter electrode was graphite,

[†]Trade name.

and the reference electrode was saturated calomel (SCE). The zinc working electrode was polished with 600 grit sandpaper, washed with methanol, and dried for at least 30 min at room temperature. The polarization was applied after a minimum of 30 min immersion of the zinc working electrode in the electrolyte. Tap water, ~1,000 ppm calcium carbonate ($CaCO_3$) solution in tap water, and ~80 to 180 ppm calcium hydroxide [$Ca(OH)_2$] solution in tap water were used as electrolyte solutions to show protection in different water chemistries. Table 1 shows the calculated corrosion rate (Equation [1]) and protection ability.

$$\text{Protection ability (\%)} = \frac{\text{corrosion rate of control} - \text{corrosion rate of sample}}{\text{corrosion rate of control}} \times 100 \qquad (1)$$

The results, presented in Table 1, show that the VpCI additive provides a high level of corrosion protection for zinc in many different water chemistries.

TABLE 1

Tafel plot data

Sample	pH	Corrosion rate (mil/y)	Protection Ability (%)
Control tap water	7.6	7.8	—
100 ppm VpCI in tap water	7.8	1.06	86.5
Control $CaCO_3$ (1,000 ppm) solution	7.8	1.8	—
100 ppm VpCI in $CaCO_3$ solution	7.9	0.24	87.2
Control $CaOH_2$ solution	8.8	33.72	—
100 ppm VpCI in $Ca(OH)_2$ solution	8.8	3.56	89.5
250 ppm VpCI in $Ca(OH)_2$ solution	8.8	0.36	98.9
Control $Ca(OH)_2$ solution	9.6	91.14	—
50 ppm VpCI in $Ca(OH)_2$ solution	9.6	26.79	70.6
250 ppm VpCI in $Ca(OH)_2$ solution	9.6	5.14	94.4

Analysis of VpCI in Water Treatment Formulations

Immersion Corrosion Test

To test VpCI additive effectiveness when used in combination with conventional water treatment programs, an immersion test was performed. VpCI additive was used at 25 wt% in two different water treatment program formulas (TF 1 and TF 2) containing a blend of antiscalants (phosphates, maleates, phosphonates, and acrylates) and azoles. These mixtures were then added to tap water at a concentration level of 2,000 ppm and an immersion test[3] was performed. The galvanized steel samples were in the solution for 10 days at 40 °C. Then corrosion products were removed by dipping for 15 s into 3% solution of hydrochloric acid (HCl) and weight loss was determined.[4] Results of this test showed that adding 25% of VpCI additive to the blend of antiscalants and azoles commonly found in water treatment formulations significantly increased the protection of galvanized steel from corrosion. Table 2 shows test results.

TABLE 2

Immersion corrosion test of VpCI additive in combination with water treatment formulations

No.	Material	Protection Ability (%)
1	Control tap water	—
2	TF 1	74
3	TF 1 + VpCI additive	94.3
4	TF 2	31
5	TF 2 + VpCI additive	94

Data indicate VpCI additive provides a high level of corrosion protection for zinc when added to conventional water treatment formulas. This work was followed by further testing on TF 1 in a cooling tower.

Testing in Pilot Cooling Tower

A cooling tower manufactured by RSD Towers, Model 005†, was used for this test. This unit provides a 16-gpm recirculation rate and has 1.5-in (38-mm) inlet and outlet diameter 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 (TDS) were between

TABLE 3

Results of pilot cooling tower test

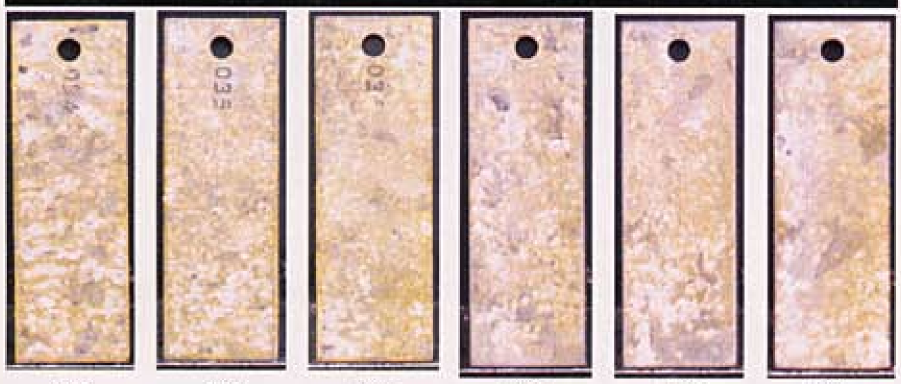
Solution Tested	Corrosion Rate (mpy)	Protection Ability (%)
TF 1 + VpCI additive	0.59	89
TF 1	4.49	—

TABLE 4

Results of immersion test of carbon steel coupons

Formulation	Concentration	Weight Loss (mg)	Weight Loss (mpy)	Average (mpy)
Control	NA	207.6	17.47	15.98
Control	NA	175.7	14.78	
Control	NA	186.6	15.70	
Formulation 1	170 ppm	12.8	1.08	0.76
Formulation 1	170 ppm	5.7	0.48	
Formulation 1	170 ppm	8.6	0.72	
Formulation 1 + VpCI	170 ppm	4.4	0.37	0.35
Formulation 1 + VpCI	170 ppm	4.2	0.35	
Formulation 1 + VpCI	170 ppm	4.0	0.34	
Formulation 2	150 ppm	145.4	12.23	11.93
Formulation 2	150 ppm	137	11.53	
Formulation 2	150 ppm	143.1	12.04	
Formulation 2 + VpCI	150 ppm	24.6	2.07	2.23
Formulation 2 + VpCI	150 ppm	37.5	3.16	
Formulation 2 + VpCI	150 ppm	18.4	1.46	

FIGURE 1



#034 (front side) #035 (front side) #036 (front side) #034 (back side) #035 (back side) #036 (back side)

Galvanized steel coupons—control.

1,250 to 1,300 ppm, and the conductivity was between 1,850 to 2,000 μS.

Samples #2 and #3 (Table 2) were evaluated in the cooling tower water. The cooling water was treated continuously as follows: 250 ppm for one week, 100 ppm for one week, and then 50 ppm during the following six weeks in both cases. Table 3 gives the average of two galvanized coupon test results.

The test in the pilot cooling tower further confirmed that adding 25% of VpCI additive to a conventional water treatment formulation significantly lowered the corrosion rate of galvanized steel.

WEIGHT LOSS/ IMMERSION TESTING

Another test of the VpCI additive in existing formulations was requested by engineers at Chem-Aqua, Inc. using tap water containing 1.008 g/L of sodium bicarbonate ($NaHCO_3$), 0.887 g/L of sodium sulfate (Na_2SO_4), 0.330 g/L of sodium chloride (NaCl), and ~4% solution of sodium hydroxide (NaOH) as needed to adjust the pH to 9.0. Polarization testing and weight loss testing were performed on two types of metals in four formulations while using the untreated solution as the control.

Coupons made from carbon and galvanized steel provided by the requesting engineers were immersed in the requested solutions as described below and tested at room temperature (~21 °C) for 10 days (240 h).

- Control solution without additional treatment
- 170 mg/L of Formulation 1 in prepared solution
- 170 mg/L of Formulation 1 + VpCI in prepared solution
- 150 mg/L of Formulation 2 in prepared solution
- 150 mg/L of Formulation 2 + VpCI in prepared solution

During the testing, the solutions were stirred at low speeds using magnetic stir plates.

Weights taken before and after testing were used to determine corrosion rates (Table 4). At the end of the testing, the galvanized steel coupons were rinsed with deionized water and then methanol (CH_3OH), hung to dry, and photographed (Figures 1 through 5). The carbon steel coupons however, were cleaned with inhibited HCl according to procedures in ASTM G1.[4] The acid cleaning solution consisted of concentrated HCl with a specific gravity of 1.18 along with 50 g/L of stannous chloride ($SnCl_2$), and 20 g/L of antimony trichloride ($SbCl_3$).

According to the results of the immersion test, all products submitted for analyses provide protection against corrosion of carbon and galvanized steel when added to water with the chemistry noted above. The effectiveness of VpCI in a water treatment formulation depends on the formulation to which it was added, and it was shown to lower the corrosion rate up to five times vs. a corresponding formulation without VpCI.

Linear Polarization Scans

Corrosion rates were obtained by using a potentiostat with corrosion software with electrodes immersed in the solutions listed in Table 5.

Corrosion rates calculated from linear polarization scans are in agreement with the results of the immersion test and confirm that addition of VpCI improves corrosion protection of the water treatment formulations.

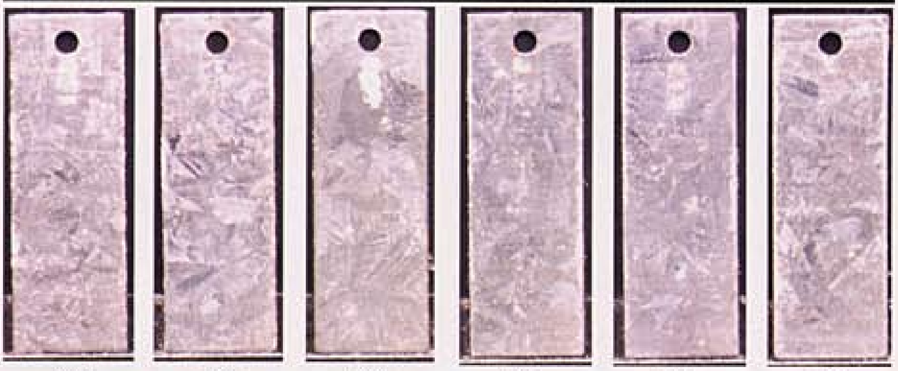
Toxicity Testing

To evaluate the toxicity of VpCI additive, two tests were performed.

Primary Skin Irritation Test

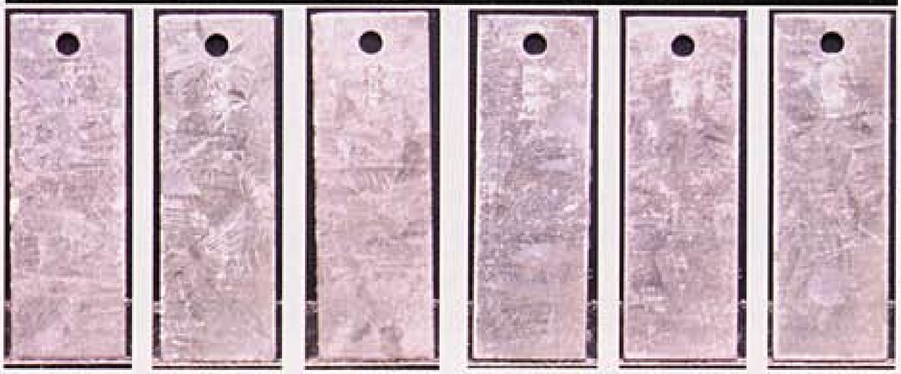
VpCI additive was applied at 4,000 ppm to the skin of rabbits and secured with wrapping for a minimum of 4 h. Observations for skin irritation were conducted at 30 to 60 min after unwrapping as well as 24, 48, and 72 h. The sum of erythema and edema scores were calculated. The final primary irritation index (PII) was 0, the best score possible in this test.[5]

FIGURE 2



Galvanized steel coupons—Formulation 1 @ 170 ppm.

FIGURE 3



Galvanized steel coupons—Formulation 1 + VpCI @ 170 ppm.

FIGURE 4

Galvanized steel coupons—Formulation 2 @ 150 ppm.

Aquatic Toxicity Test

VpCI was also tested for aquatic toxicity with several species. Table 6 shows the levels tested.[6]

The theoretical median lethal dose (LD_{50}) for rats has been calculated to be >4,000 ppm based on ingredients present. The chemical oxygen demand

FIGURE 5

#021 (front side) | #022 (front side) | #023 (front side) | #021 (back side) | #022 (back side) | #023 (back side)

Galvanized steel coupons—Formulation 2 + VpCI @ 150 ppm.

TABLE 5

Results of linear polarization scans

Sample	Corrosion Rate (mpy)	
	Carbon Steel	Zinc
Control (prepared solution)	22.0	11.50
170 ppm of Formulation 1 in prepared solution	8.17	6.84
170 ppm of Formulation 1 + VpCl in prepared solution	3.52	5.87
150 ppm of Formulation 2 in prepared solution	7.47	4.625
150 ppm of Formulation 2 + VpCl in prepared solution	5.34	2.99

TABLE 6

Results of toxicity testing of VpCI

Species	NOEC	LOEC	LC_{50}	IC_{25}
M. Beryllina	1,000 ppm	2,500 ppm	—	—
M. bahia	600 ppm	1,000 ppm	—	—
Fathead minnow	—	—	1,700 ppm	140 ppm
C. dubia	—	—	1,100 ppm	90 ppm

(COD) at 100 ppm has been tested in the range of 81 ppm according to the U.S. Environmental Protection Agency (EPA) method 410.1.[7]

The data show that the VpCI additive is safe for handling and use in cooling water treatment programs. At concentration of use it remains safe for many species, allowing discharge according to local authorities.

Conclusions

The advantage of using a VpCI additive in cooling water was tested with various methods including immersion tests, Tafel plots, linear polarization scans, and cooling tower tests. These tests all show the ability of the VpCI additive to protect galvanized steel against corrosion. The VpCI additive is safe, environmentally acceptable for use, and can be added to traditional water treatment programs to significantly improve the corrosion protection of galvanized steel.

References

1 "White Rust: An Industry Update and Guide Paper," AWT, 2002.

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

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

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

5 Lab Project # 9693, ViroMED Biosafety Laboratories.

6 Environmental Enterprises, USA, and Environmental Consulting & Testing.

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

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