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Anti-Corrosion Building Blocks for Open Recirculation Loop Cooling Systems

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ABSTRACT

Cooling systems are crucial components of many processing and manufacturing plants. It is important to maintain these systems and keep them in good working condition. One problem faced during maintenance is corrosion. Corrosion mitigation is often time consuming and costly. The goal of this paper is to show the effectiveness and advantages of Vapor Phase Corrosion Inhibitors (VpCIs) in the protection of different metals of open recirculating loop cooling systems including copper and galvanized steel. VpCI materials discussed in this paper are environmentally friendly, and can be made from biodegradable and sustainable resources. Laboratory test results, pilot test results, and field results will be presented.

Key Words: Corrosion, Cooling, Open Recirculating Loop, Water Treatment

INTRODUCTION

The latest study by the Federal Highway Administration estimated the annual direct costs of corrosion to be $276 billion - approximately 3.1% of the nation's Gross Domestic Product (GDP). Several manufacturing sectors were surveyed, including the food processing industry with $2.1 billion cost, pulp & paper industry with a $6 billion cost, and a grouping of chemical, petrochemical and pharmaceutical industries with a $1.7 billion cost[1].

Cooling systems contain several types of metals including copper, steel, galvanized steel, and aluminum. Galvanizing, or the coating of zinc onto steel, is widely used in open loop cooling systems for its ability to protect steel from corrosion and its cost-effectiveness. This material can offer 20 years or more life expectancy when maintained properly. However, especially when pH is over 8.2, corrosion may begin and the appearance of "white rust" is seen. This oxidized zinc is no longer protecting the steel and the lifespan of the metal system would therefore be significantly reduced[2].

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Vapor-phase Corrosion Inhibitors (VpCI) are one type of inhibitor to combat the corrosion problems faced by water treatment providers. VpCIs have been used for a long time; however, some of them could be aggressive to non-ferrous metals and especially yellow metals[3]. 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 researches, but lately environmental regulations based on toxicity data have severely restricted the use of triazoles.[4]

Recent developments in VpCI technology proved that vapor corrosion Inhibitors can be successfully used for the protection of multi-metal systems including water treatment and this topic will be discussed throughout this paper.

EXPERIMENTAL PROCEDURE

The experimental effort was designed to show the effectiveness of several VpCI Building Blocks to prevent corrosion to several types of metals, not only ferrous, but 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 contains triazole and can be used by itself or as a part of a treatment to enhance the corrosion protection.

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 with triazole added for the protection of yellow metals.

VpCI D is a blend of the protein portion of soy beans and sequestering agents. 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 interface, exposing the reactive site of their amino acid chains.

Electrochemical Testing

Tests were performed in conditions based on recommendations of ASTM G-5[5] using a Potentiostat/Galvanostat "Versastat" with 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 minutes immersion of working electrode in the electrolyte.

The working electrode (made of zinc, steel, etc.) was polished with 600 grit sand paper, 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 G-31[6]. Sanded and methanol cleaned metal panels were immersed in containers filled with water-based solutions/electrolytes with or without added treatment ('Control'). After the test, the weight loss was determined or panels were visually evaluated for the presence of corrosion after cleaning according to ASTM G-1.[7]

Tests in Pilot Cooling Tower

Various treatments were tested in the Model 005 cooling tower manufactured by RSD Towers. This unit provides 16 GPM recirculation rate and has 1.5 inch inlet and outlet diameter. The test was performed in tap water with 2.3-2.5 cycles of concentration and a temperature 45-50^oC. The pH of the system was between 8.6 and 8.8, the TDS in the basin was between 1250-1300ppm; and the conductivity level was approximately 1850-2000uS.

Corrosion coupons were placed in contact with the water passing through the tower and corrosion rates calculated using the average values from coupons and the formula

$$\text{Corrosion Rate} = (K * W)(A*T*D) \qquad \text{(Equation 1)}$$

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

Toxicity Testing

Primary Skin Irritation Test: The VpCI Building Blocks were applied to skin of rabbits and secured with wrapping for a minimum of 4 hours. Observations for skin irritation were conducted at 30 to 60 minutes after unwrapping as well as 24 hr, 48 hr, and 72 hr. The sum of erythema and edema scores was calculated.[8,9]

Aquatic Toxicity Test: The VpCI Building Blocks were tested for aquatic toxicity with several species. These tests included 48-hour static-renewal Daphnia pulex and Pimephales promelas definitive tests which were performed in synthetic moderately hard freshwater according to EPA/600/4-90/027F and 48-hour static-renewal acute M. beryllina and M. bahia definitive tests which were performed in synthetic seawater according to EPA-821-R-02-012. These tests found 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 Tables and Figures below.

To compare the ability of VpCI A and D to protect copper, aluminum and galvanized steel against corrosion in static conditions, half immersion corrosion tests in tap water were performed (Table1). The data shows that the VpCI products outperform their conventional counterpart in protection of copper, aluminum and galvanized Steel.

Table 1
Half-Immersion Test of VpCI A and VpCI D at Room Temperature for 72 hours

Product	Metal	Observations	Metal	Observations	Metal	Observations
Conventional, 2000ppm	Copper	corrosion	Aluminum	corrosion	Galvanized Steel	corrosion
VpCI A, 2000ppm	Copper	no sign of corrosion	Aluminum	no sign of corrosion	Galvanized Steel	no visible corrosion
2000ppm VpCI D, 2000ppm	Copper	slight corrosion	Aluminum	no sign of corrosion	Galvanized Steel	no visible corrosion
Control (Tap Water)	Copper	slight corrosion	Aluminum	no sign of corrosion	Galvanized Steel	no visible corrosion

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 2 show that VpCI A provides a high level of corrosion protection for Zinc in the presence of $CaCO_3$ and high pH level. Protection Ability was calculated using the equation

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

Table 2
VpCI A Corrosion Rate Data Calculated from Tafel Plots

Treatment	pH	Zinc Corrosion Rate mil/year	Protection Ability, %
Control Tap Water	7.6	7.8	-
100ppm VpCI A in Tap Water	7.8	1.06	86.5
Control $CaCO_3$ (1000ppm) solution	7.8	1.8	-
100ppm VpCI A in $CaCO_3$ solution	7.9	0.24	87.2
Control $CaOH_2$ solution	8.8	33.72	-
100ppm VpCI A in $Ca(OH)_2$ solution	8.8	3.56	89.5
250ppm VpCI A in $Ca(OH)_2$ solution	8.8	0.36	98.9
Control $Ca(OH)_2$ solution	9.6	91.14	-
50ppm VpCI A in $Ca(OH)_2$ solution	9.6	26.79	70.6
250ppm VpCI A in $Ca(OH)_2$ solution	9.6	5.14	94.4

Table 3 and Table 4 present the results of immersion testing and show VpCI A provides a high level of corrosion protection for carbon steel and galvanized steel when added to conventional water treatment formulas. The galvanized steel samples were in the solution for 10 days at 40℃. Thereafter corrosion products were removed by dipping for 15 seconds into 3% solution of hydrochloric acid and weight loss was determinated.[7]

Table 3
Carbon Steel Immersion Test Results of VpCI A Incorporated into Formulations

Treatment	Concentration	Weight Loss (mg)	MPY	Average MPY
Control*	n.a.	207.6	17.47	**15.98**
Control*	n.a.	175.7	14.78	
Control*	n.a.	186.6	15.70	
TF 1	170ppm	12.8	1.08	**0.76**
TF 1	170ppm	5.7	0.48	
TF1	170ppm	8.6	0.72	
75% TF 1 + 25% VpCI A	170ppm	4.4	0.37	**0.35**
75% TF 1 + 25% VpCI A	170ppm	4.2	0.35	
75% TF 1 + 25% VpCI A	170ppm	4.0	0.34	
TF 2	150ppm	145.4	12.23	**11.93**
TF 2	150ppm	137	11.53	
TF 2	150ppm	143.1	12.04	
75% TF 2 + 25% VpCI A	150ppm	24.6	2.07	**2.23**

* Tap water containing 1.008 g/L of sodium bicarbonate, 0.887 g/L of sodium sulfate, 0.330 g/L of sodium chloride and ~4% solution of NaOH as needed to adjust the pH to 9.0 as requested by customer.

Table 4
Galvanized Steel Immersion Corrosion Test of VpCI A Incorporated into Formulations

Treatment	Protection Ability, %
Control (Tap Water)	-
TF 1	74.0
75% TF 1 + 25% VpCI A	94.3
TF 2	31.0
75% TF 2 + 25% VpCI A	94.0

Corrosion rates calculated from linear polarization scans, as shown in Table 5, are in agreement with the results of the immersion test, confirming that the addition of VpCI A improves the corrosion protection of the water treatment formulations submitted.

Table 5
Results of Linear Polarization Scans of Formulations using VpCI A in Combination with Water Treatment Formulations

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

Cooling tower testing commenced on TF1 with and without VpCI A at 250 ppm for 1 week, 100 ppm for 1 week and then 50 ppm for 6 weeks to see the protection of Galvanized Steel. This testing further confirmed that adding 25% of VpCI A to a conventional water treatment formulation significantly (5 times) lowered the corrosion rate of galvanized steel as seen in Table 6. The photos of the coupons used can be seen in Figures 1-5.

Table 6

Result of Pilot Cooling Tower Test using Formulation With and Without VpCI A addition

Treatment	Average Corrosion Rate, mpy	Protection Ability, %
TF 1	4.49	-
75% TF 1 + 25% VpCI A	0.59	89

Figure 1. Galvanized Steel Coupons – Control

Figure 2. Galvanized Steel Coupons – Formulation 1 @ 170ppm

Figure 3. Galvanized Steel Coupons – Formulation 1 + VpCI A @ 170ppm

VpCI B was tested specifically as a replacement for triazole treatments used to protect copper, as shown in Table 7 below. Triazole is more effective in corrosion protection of copper, but considering that systems are usually made from different metals which triazole does not protect, instead of the addition of this environmentally questionable product, it my 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 its environmental issues become more stringent.

Table 7
Corrosion Protection Provided to Copper by VpCI B

Treatment	**Copper Corrosion Rate, mpy**	**Protection Ability, %**
VpCI B, 1000ppm	0.02525	99.65
Triazole , 500 ppm	0.0098	99.86
Control (tap water)	7.138	-

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 to a copper/nickel alloy as shown in Table 8.

Table 8
CDA 715 (Copper:Nickel = 30:70) Immersion Corrosion Test of VpCI C

Treatment	**Initial Weight (g)**	**Final Weight (g)** (After 3 weeks in 40C oven)	**Protection Ability, %**
Control (Tap Water)	14.7145	14.7135	-
1000ppm VpCI Building Block C	14.6980	14.6978	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 250ppm for seven days, 100ppm for seven days, and 50ppm for 80 days. Make-up water was also treated with 5ppm of an oxidizing biocide. Results show that VpCI C provides additional corrosion protection to existing formulations as shown in Table 9.

Table 9
Cooling Tower Results of Commercial Formula with and without VpCI C Addition

Treatment	**Corrosion Rate, mpy (Based on average weight loss of coupons)**		
	Carbon Steel, SAE 1010	**Copper, CDA 110**	**Hot Dipped Galvanized Steel**
Commercial	6.34	0.00	4.49
Commercial 10%VpCI C	0.81	0.00	1.15
Additional Protection Ability, %	87.2	-	74.4

A variety of metals were also used in cooling tower tests of VpCI D in conjunction with conventional water treatment products. Results in Table 10 show that VpCI D can be used alone to provide protection or can be added to formulations for additional corrosion protection.

Table 10
Pilot Cooling Tower Test Results of Formulations with and without VpCI D Addition

Treatment	**Carbon Steel Corrosion Rate, mpy**	**Protection Ability, %**	**Galvanized Steel Corrosion Rate, mpy**	**Protection Ability, %**	**Copper Corrosion Rate, mpy**
Conventional 50ppm + Oxidizing Biocide	1.3	79.5	2.5	44.3	0.051
VpCI D @ 10ppm + Oxidizing biocide	0.9	85.5	0.77	82.9	0
Conventional+10% VpCI D at 50ppm (~5ppm VpCI D) +Oxidizing Biocide	1.13	82.2	1.44	67.9	0.011

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 11 below.

Table 11
Toxicity Testing Results of VpCI Building Blocks

Test	Species	VpCI A	VpCI C	VpCI D
Mammalian Toxicity Test 336 hr	Rattus sp.	-	Theoretical LD_{50}>4000 mg/kg rat	-
Fresh Water Species 48-hr static renewal test (EPA/600/4-90/027F)[12,13]	D.pulex	-	NOEC=10,000ppm LOEC=>10,000ppm	TBD
Fresh Water Species 48-hr static renewal test (EPA/600/4-90/027F)[12,13]	P. promelas	-	NOEC=10,000ppm LOEC=>10,000ppm	TBD
Sea Water Species 48-hr static renewal test (EPA-821-R-02-012)[11,14]	M. bahia	NOEC=600ppm CTS LEOC=1000ppm CTS	-	NOEC=360ppm LOEC=600ppm 48-hour LC50=282ppm
Sea Water Species 48-hr static renewal test (EPA-821-R-02-012)[11,14]	M. Beryllina	NOEC=1000ppm CTS LOEC=2500ppm CTS	-	NOEC=<1296ppm LOEC=1296ppm 48-hour LC50=2630ppm
Fathead Minnow[10]	Fathead Minnow	LC_{50}=1659 IC_{25}=141.2	-	-
C. dubia[10]	C. dubia	LC_{50}=1051 IC_{25}=86.7	-	-
Skin Testing[8,9]	Rabbit	0 at 4000ppm	0 at 2000ppm	-
COD, EPA method 410.1.[15]	-	~81ppm	-	-

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 in various water chemistries. They have been shown to be effective not only for ferrous metals, but also for non-ferrous metals of copper, zinc, etc., 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.

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