METHODOLOGY OF VCI'S FOR WATER TREATMENT

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ABSTRACT

Four formulations were suggested to reduce the corrosion rate when added to both fresh and salt water. Formulated according to VCI technology, these products include inhibitors for multi-metal protection in liquid, vapor and interface liquid/vapor phase.

The performance of the products was evaluated at different temperatures in the immersion test and electrochemical techniques.

The synergistic effect of the components in formulations was studied using infra-red spectroscopy.

The protection ability vs. concentration was studied for the additive for an open loop cooling system (OCA).

Keywords: vapor corrosion inhibitors (VCI), water treatment additives, electrochemical techniques, salt oxicarbonic acid, aminocarboxylate, water soluble sulfonate, organophosphonates, triazoles.

INTRODUCTION

Corrosion still remains a significant problem for many industrial systems where water is used. Industry probably uses more water for cooling than for all other purposes combined. Condensers, heat exchangers, cookers, engines, compressors, etc., all need cooling water and the cooling-system maintenance can be very costly unless the water is treated to prevent corrosion, deposits, and biological growths. The most common methods of reducing the danger of corrosion are using non-metallic materials, corrosion resistant alloys (stainless steel) or the purification of process water (using Deionized water instead of tap or sea water, etc.). One of the most economical methods of corrosion protection is adding an effective corrosion inhibitor system. Many papers have been published about usage of Volatile Corrosion Inhibitors (VCIs) in different industries [1-5]. The goal of this work is to distinguish the effectiveness of four new additives which provide protection in salt and fresh water.

EXPERIMENTAL

Electrochemical analysis was performed using a three electrode system [6]. The carbon steel working electrode, a saturated calomel reference electrode and high purity graphite counter electrodes were used in the corrosion sell. Measurements were taken using Potentiostat/Galvanostat “Versastat” with corrosion software model 352/252 SoftCorr™ . The working electrode was polished with a 600 grit sand paper, washed with methanol and dried for 1 hour. The polarization curves were obtained ½ hour after the working electrode was immersed in the solution using Tafel Technique at room temperature. Stearing with a magnetic stear provided 200 rpm (rotations per minute).

Corrosion rate monitoring was performed using a Corrater 9030 corrosometer, Rohrback Casasco system with electrodes from carbon steel. The electrodes were polished with 600 grit sand paper, washed with methanol, and dried for one hour. The electrodes were then immersed in the solution.

Infra-red spectra were obtained using FT-IR spectrometer, Paragon 1000 Perkin Elmer. The samples for the test were concentrated and cast on silver bromide windows. The solvent was methanol.

Corrosion tests were performed on immersed and half-immersed carbon steel and copper panels [7]. Carbon steel panels were from cold rolled steel, ASTM C1010 provided by the Q Panel Company. Both sides of the copper panels (CDA110) were sanded with 280 grit sand paper. The panels were washed with methanol prior to testing. The tests were performed at temperatures of 50^{o}C and room temperature.

Artificial “sea water” was prepared from “Instant Ocean,” a synthetic sea salt.

All additive packages are technical grade and free from chromate, nitrites and zinc. They are environmentally friendly and easily disposed.

RESULTS AND DISCUSSION

SWI (salt water inhibitor) was designed to protect metals in brines, hard and salt waters. The effectiveness of it in liquid phase is evaluated from the electrochemical analysis and immersion testing. The performance of vapor phase inhibiting effect is evaluated by half-immersion testing. The formulation includes the contact corrosion inhibitor, salt of oxicarbonic acid, which acts as surface modified and oxygen scavenger, aminocarboxylate which provide the protection in vapor phase and triazole.

The data (Table 1) show that only the complete composition (contact and vapor inhibitor, oxygen scavenger) provides three phase protection. Figure 1A shows that adding SWI to salt water influences both the anodic and cathodic reactions. Figure 1B shows that this formulation provides the similar protection in "sea" water.

CLA (additive for closed loop cooling system) was designed to protect re-circulating cooling systems. FWI (fresh water inhibitor) was designed as a "building block" to water treatment formulations, and it also protects steel and non-ferrous metals in tap water at room and elevated temperatures. It is also compatible with a majority of anti-scalants and biocides. The film-forming contact inhibitor water-soluble sulfonate (A), amino-carboxylate (B) as a VCI and triazole are the main protective components of CLA and FWI (fresh water inhibitor).

Table 2 shows that blending the two major components of CLA and FWI sulfonate (A) aminocarboxylate (B) gives a synergistic effect of protection in liquid phase. Corrosion rates were calculated from polarization curves.

To explain this data, IR spectra were obtained (Figure 2). The major ingredients in CLA and FWI have characteristic peaks: 1420, 1580-1610 cm^{-1} and 1380, 1450 cm^{1}, respectively. Final product (FWI) has the same peaks (1420, 1580-1610 cm^{1}) like the first ingredient, but almost doesn't have transmission peaks in an area 1380, 1450cm^{-1}. In the same time peak at 1420 cm^{-1} and 1580cm^{-}1 changed their shape, building more asymmetric peaks, which can be explained as a shifting of characteristic peaks of the second ingredient in an area with higher frequency and they are covered with peaks 1420 cm^{-1} and 1580 cm^{-1} respectively.

The performance of the FWI and CLA is shown in Table 3 and Figure 3. The polarization curves (Figure 3) obtained for CLA and FWI show that they affect anodic and cathodic reaction but mostly anodic as it moves the corrosion potential in a positive direction. The data displayed in Table 3 shows a high level of protection for immersed and half-immersed copper and carbon steel in tap water at room temperature and at 50^{o}C.
OLA (additive for open loop cooling systems) was designed for open loop cooling systems. It contains organophosphonate, triazole, biocides, and an anti-scalant agent. The data obtained from the study of OLA using electrochemical methods (corrosion monitoring and polarization

curves are in a good agreement and show that OLA provides protection even at a concentration level of 50 ppm (Figure 4, Table 4). The components of this formulation influence mainly anodic reactions and nobilize the corrosion potential.

This formulation provides excellent protection to carbon steel and copper when immersed or half-immersed in tap water at room and elevated temperatures of 50^{o}C (Table 3).

Analyzing the above mentioned allowed one to conclude that to formulate additives which will provide three phase protection (liquid-vapor interface, vapor phase) a balanced combination of vapor phase and contact inhibitors should be used. The ratio of components in the formulation should provide a uniform activity at the metallic surface immersed in the solution, at and above the waterline.

Table 1

SWA: Protection ability of inhibitor for brines and salt water. Tested for carbon steel and copper. The solution used 3.5% NaCl + 0.5% inhibitor.

Immersed

Material	**Time Before Corrosion (days)**
Contact inhibitor + oxygen scavenger	10+
SWA	10+/10+*
Control	<1/<1*

* The upper data shows protection to carbon steel, the lower for copper (carbon steel/copper).

Half-Immersed

	Time Before Corrosion (Days)		
Material	In solution	Waterline	Above Waterline
Contact inhibitor + oxygen scavenger + VCI	10+	10+	**7**
SWA	10+/10+*	10+/10+*	**7+**/10+*
Control	<1/<l*	<1/<1*	<1/,1*

* The upper data shows protection to carbon steel, the lower for copper (carbon steel/copper).

Table 2

Synergistic interaction of the components within FWI and CLA.

Material	Corrosion rate, mmpy x 103
500 ppm A + tap water	11.45
500 ppm B + tap water	64.11
250 ppm A + 250 B + tap water	1.457

Table 3

Study of the performance of the formulations 2, 3 and 4 in tap water.
Concentration level 0.1% by mass

Copper (Immersed)

	Time before corrosion (days)	
Material	**Ambient Temperature**	**50^oC**
CLA	60+	60+
OLA	60+	60+
FWI	60+	60+

Table 4

Electrochemical study of the effectiveness of OLA in tap water.

Concentration level, ppm	Polarization curves		Corrosion monitoring	
	Corrosion rate, mmpy x 10^3	**Protection power, Z%**	**Corrosion rate, mmpy**	**Protection Power Z, %**
1000	14.4	86	0.09	98.5
100	16.64	84	0.60	90.0
50	50.78	50	2.00	67.7
0	101.2	-	6.00	-

$$Z = \frac{CR\ w/o\ inh - CR\ w/\ inh}{CR\ w/o\ inh} \times 100\%,$$ where

CR w/o inh = Corrosion rate in tap water
CR w/inh = Corrosion rate in tap water when inhibitor added

Carbon Steel (Immersed)

	Time before corrosion (days)	
Material	**Ambient Temperature**	**50^{o}C**
CLA	40+	40+
OLA	40+	40+
FWI	40+	40+

Carbon Steel (Half-immersed)

	Time before corrosion (days)	
Material	**Ambient Temperature**	**50^oC**
CLA	40+	20+
OLA	40+	20+
FWI	40+	20+

CONCLUSION

VCI technology was used to develop four new non-toxic, environmentally friendly effective corrosion inhibitors for multi-metal protection in salt and fresh water. Their performance was confirmed using electrochemical and corrosion test methods.

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7. ASTM G 31-72 “Standard Practice for Laboratory Immersion Corrosion Testing of Metals”

I/area (A/cm^2)

Figure 1A. Polarization curves for carbon steel in 3.5% NaCl with and without 0.5% SWI

1 = with SWI
2 = Control

I/area (A/cm^2)

Figure 1B. Polarization curves for carbon steel in artificial sea water with and without 0.5% SWI

1 = with SWI

2 = Control

Figure 2. FT-IR spectrum of the FWI and its ingredients

fwi:	FWI______________	96/12/05
b:	B ______________	96/12/05
a:	A ______________	96/12/05

Figure 3. Polarization curves for carbon steel in tap water with and without 0.1%

1 = FWI

2 = CIA

3 = Control

Figure 4. Polzrization curves for carbon steel in tap water with and without OLA

1 = 0.1% OLA

2 = 0.01% OLA

3 = 0.005% OLA

4 = Control