

## **INVESTIGATION OF BIO-BASED AROMATIC ACIDS AS CORROSION INHIBITOR**

Ming Shen, Alla Furman, Rita Kharshan  
Cortec Corporation  
4119 White Bear Pkwy  
St Paul, MN 55110

Interest in corrosion mitigation utilizing renewable and biodegradable raw materials is quickly on the rise. A number of plant materials as corrosion inhibitor have been reported. In many cases, however, preparation of corrosion inhibitor from these source materials is laborious so industrial scale application is difficult. The work reported here utilizes industrial available bio-based materials. Bio-based aromatic acids, such as vanillic acid, ferulic acid, cinnamic acid, and mandelic acid, were studied for their potential as industrial corrosion inhibitors in vapor phase, in various water-based electrolytes, and in vapor/electrolyte inter phase. Simple preparations of these bio-based aromatic acids demonstrated that some of these materials possess ability of vapor phase corrosion inhibition (VCI). Some preparations of the bio-based acids showed potential as additive for mild steel protection in immersion or partial immersion applications in water-based electrolytes. Synergistic combination of different preparations showed superior performance than individual material. Patents of the United States and other countries are pending on this work.

Key words: corrosion inhibitor, renewable, biodegradable, bio-based, aromatic acid, VCI, immersion, partial immersion, mild steel

### **INTRODUCTION**

The latest estimate of annual costs of corrosion in the United States is \$1 trillion<sup>1</sup>, more than 3 times of the amount reported by NACE in 1998<sup>2</sup>. To combat corrosion, approximately \$121 billion per year were spent on methods to prevent and control corrosion in 1998. Of this total, \$0.4 billion were spent on vapor corrosion inhibitors (VCI). New technologies and raw materials derived from renewable, biodegradable, and non-hazardous raw materials are of particular interest for use as corrosion inhibitor chemicals. As government policy continues to promote green alternatives to petrochemicals, the availability and utility of agricultural or forestry products and by-products will become economically advantageous.

A wide range of plant materials as corrosion inhibitor have been reported, from vegetable and fruit such as red onion<sup>3</sup>, coffee<sup>4</sup>, papaya leaves<sup>5</sup>, and banana peels<sup>6</sup>, to many varieties of plant leaves<sup>7,8</sup>. In many cases, however, the source materials are not commercially available, and the preparation of corrosion inhibitor from these source materials is laborious. The adoption of these types of “green” inhibitors is difficult on an industrial scale.

The work described here utilizes industrial available bio-based materials. Particularly, a group of bio-based aromatic acids was studied for their potential as industrial corrosion inhibitors in vapor phase, in various water-based electrolytes, and in vapor/electrolyte interphase. This group of bio-based aromatic acids was chosen in part because they are derivatives of natural lignin, the second most abundant natural polymer in the world, surpassed only by cellulose<sup>9</sup>. Table 1 summarizes the fundamental properties of this group of acids

**Table 1**  
**Fundamental Properties of the Bio-based Aromatic Acids Studied**

Name	MW	state
Acid A	168	White powder
Acid B	148	White powder
Acid C	194	White powder
Acid D	152	White powder

Lignin derivatives have been reported to have inhibitive properties in aqueous phase<sup>10</sup>. Protection of cinnamic acid to mild steel in vapor phase<sup>11</sup> and in acidic medium<sup>12</sup>, vanillic acid to aluminum in acidic solution<sup>13</sup>, and ferulic acid to mild steel in near neutral solution<sup>10</sup>, have appeared in literatures.

In our study, the biobased aromatic acids were prepared simply as salts using liquid ammonia and other alkaline materials. Corrosion inhibiting properties of the ammonium salts of the biobased aromatic acids are reported, and compared with their petroleum-based counterparts, in this paper. Interestingly, ammonium salt of acid A, and of acid C, exhibited volatile corrosion inhibition property; while ammonium salt of B, and of D, did not. In addition, ammonium salts of acid A, of acid C, and of acid B, showed excellent protection to mild steel in partial immersion test, lending them worthy candidates as “green” inhibitor for water treatment industry to meet discharge regulations with ease. When ammonium salts of acid B and of acid A, or of acid B and of acid C, were combined, a synergistic protection effect was shown in hydrostatic testing using salt water. Hydrotesting, or hydrostatic testing, is a process in which pressure vessels such as pipelines, plumbing, gas cylinders, boilers and fuel tanks are tested for strength and leaks. When water is used as testing liquid, corrosion protection of the vessel under the testing, particularly those constructed of carbon steel or cast iron, must be considered. The protection challenge is greater when salt water is used due to the aggressive chloride electrolyte. The protection is needed when the vessel is filled with salty water, and when the vessel is drained off the liquid but still exposed to salt residue, oxygen and humidity left by the testing.

## **MATERIALS AND EXPERIMENTAL PROCEDURES**

### **Preparation of Ammonium Salt of Aromatic Acids**

Aromatic acids of A (97%), B (99%), C (99%), and (99%) were purchased from Sigma Aldrich<sup>†</sup>. A salt solution was prepared for each acid by reacting with liquid ammonia (30%) to pH 9.5 to 10.5. Each salt solution contained 15% salt solid.

### **Metal Specimens**

SAE<sup>♦</sup> 1010 (AISI1010) cold rolled carbon steel panels (1x4" or 2.5x10.2cm) were used in immersion test and partial immersion test. AISI1010 carbon steel plugs (D=1.5cm, H=1.3cm) were used for Vapor Inhibition Ability (VIA) test.

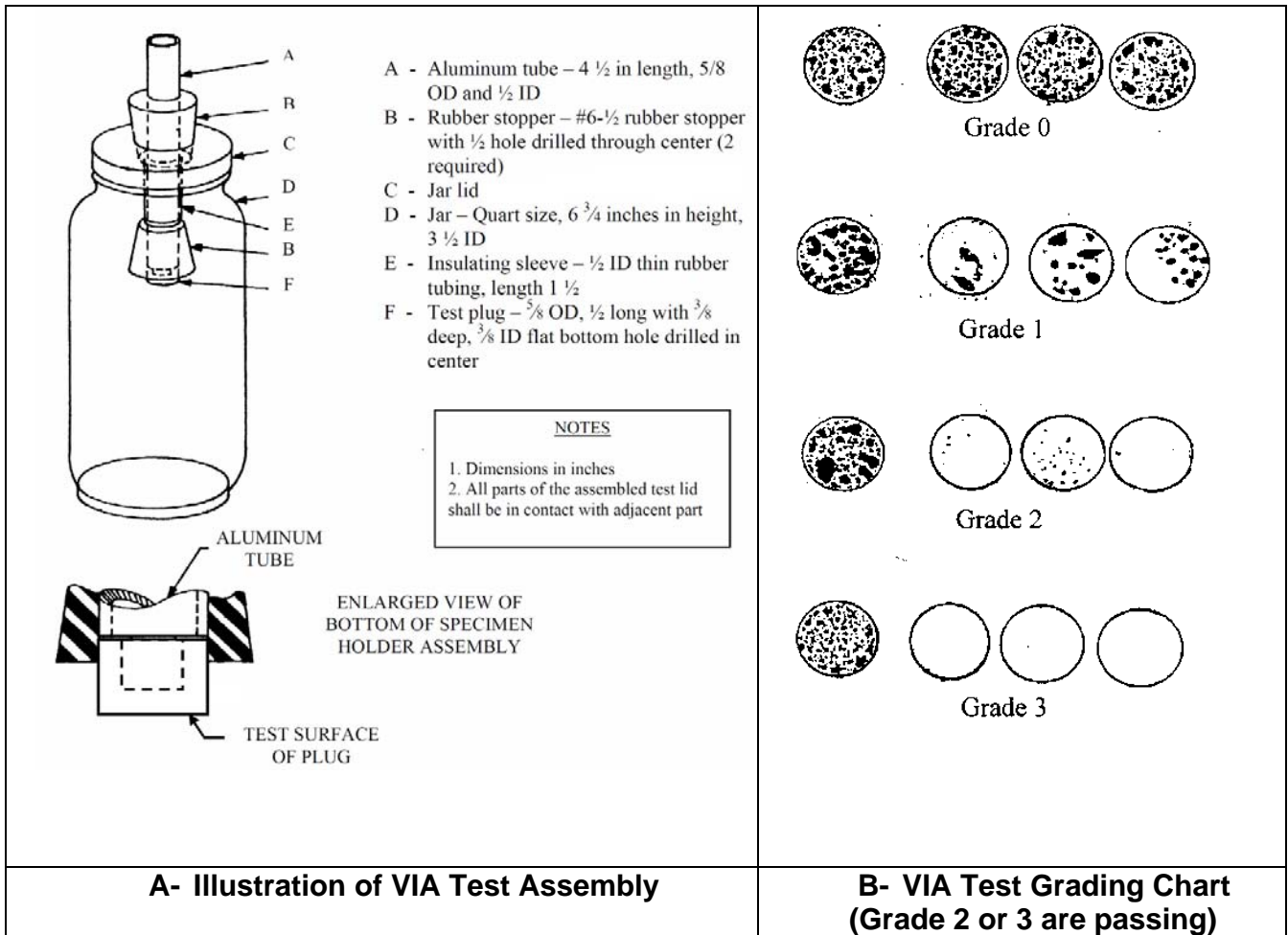
### **Evaluating Vapor Inhibiting Ability (VIA)**

VIA Test evaluates a product's ability to protect metal from corrosion without being in direct contact. VIA test described here is based on the Military Standard MIL-STD 3010B, Method 4031<sup>14</sup>. An illustration of the VIA test assembly is shown in Figure 1A. A test sample (in a dish if liquid or powder) is placed into a quart-sized glass jar. The jar is capped with a lid that contains a freshly polished and cleaned carbon steel plug (AISI1010) for 20 hours at ambient temperature. A relative humidity of nearly 100% is then created in the jar (via addition of 3% glycerol in water) for 2 hours at ambient temperature, followed by another 2 hours at 40°C. After 24 hour exposure, the plug is removed from the jar and its polished surface is inspected and rated on a scale of 0 to 3, where 0 is heavily corroded (no corrosion inhibition), and 3 exhibits no visible corrosion (good inhibiting effects) (see VIA Grading Chart, Figure 1B). The test is run in triplicate. The control is a plug exposed in a jar without inhibitor.

---

<sup>†</sup> Trade name

<sup>♦</sup> Society of Automotive Engineers International, Troy, Michigan



**Figure 1: Illustration of VIA Test**

**Immersion Test and Partial Immersion Test**

Immersion test and partial immersion test was carried per ASTM<sup>^</sup> G31<sup>15</sup>

Immersion and partial immersion were carried out either in tap water or in salt water (3.5% NaCl).

Cleaning of metal panels after testing was per ASTM G1<sup>16</sup>.

Weight loss method was used to assess the protection (%Z) in immersion test.

$$\%Z = 100 \times (C_c - C_i) / C_c$$

where

C<sub>c</sub> - weight loss without inhibitor

C<sub>i</sub> - weight loss with corrosion inhibitor

**Corrosion in Hydrostatic Testing**

Corrosion of carbon steel during and after hydrostatic testing using salt water was simulated in lab setting by immersing a AISI 1010 carbon steel panel in salt water (3.5% NaCl) in a bottle, with or without inhibitor additive, for 6 hours, followed by draining off most of the testing liquid but keeping the steel panel in the capped bottle for 7 days. A spacer was placed between the bottom of the panel and the residue liquid, Figure 2. At the end of testing, the panels were cleaned according to the procedure of ASTM G1.

<sup>^</sup> ASTM International (ASTM), 100 Barr Harbor Dr., West Conshohocken, PA 19428-2959.

In addition to visual inspection and photo recording, weight loss method was used to assess the protection (%Z) in hydrostatic testing. The weight loss was calculated by subtracting a panel's weight at the end of a testing (after being cleaned) from the panel's initial weight before it was immersed in the hydro testing liquid:

$$\%Z = 100 \times (C_c - C_i) / C_c$$

where  $C_c$  - weight loss without inhibitor  
 $C_i$  - weight loss with corrosion inhibitor



**Figure 2: Setup of Corrosion Testing in Hydro Testing**







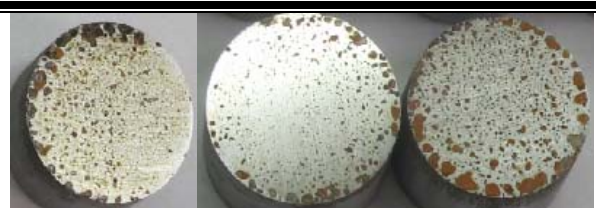
## RESULTS

### Vapor Inhibition Ability (VIA)

Vapor Inhibition Ability (VIA) test showed that ammonium salt of A, and of B, had vapor inhibition ability. Their vapor phase protection was excellent at 1g solution (equivalent to 0.15g active salt), and acceptable at 0.5g solution (0.075g salt), Table 2. Ammonium salt of cinnamic, however, didn't show vapor protection ability.

**Table 2**  
**VIA Test on Solution of Ammonium Salt of Aromatic Acids**

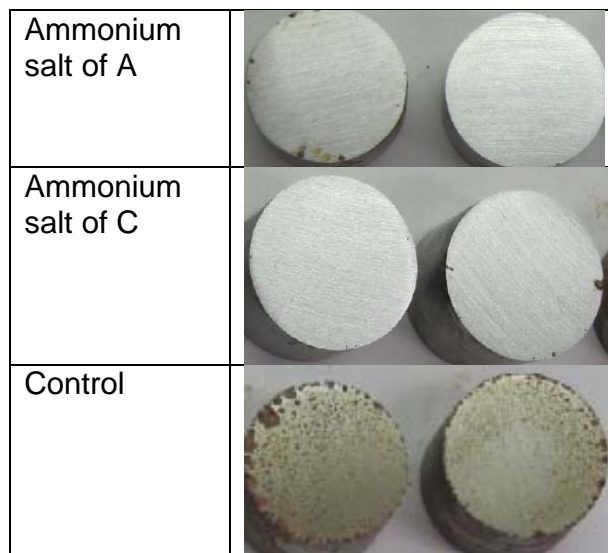
Specimen	Plugs	VIA Grade pass/fail

Ammonium salt of acid A (1g solution/0.15g salt)		3,3,3 Pass
Ammonium salt of acid C (1g solution/0.15g salt)		3,3,3 Pass
Ammonium salt of acid B (1g solution/0.15g salt)		0,0,0 Fail
Ammonium salt of acid D (1g solution/0.15g salt)		0, 2,2 Fail
Ammonium salt of acid A (0.5g solution/0.075g salt)		2,2,2 Pass
Ammonium salt of acid C (0.5g solution/0.075g salt)		2,3,3 Pass
Control		0,0,0 Fail

When the ammonium salt of acid A, and of acid B, was applied onto a piece of paper (2x5") and dried (10min, 40C), VIA test showed that the paper also exhibited VIA, Table 3, indicating that the salt solid possessed VIA.

**Table 3**  
**VIA Test on 0.15g Dried Salt**

Specimen	Test Plugs
----------	------------



### Immersion in Tap Water

Immersion in tap water containing 0.75% (wt) ammonium salt of A, of B, and of C, showed that the respective salt provided protection of 99%, 99%, 99%. Ammonium salt of D, however, provided only modest protection of 45%, Table 4. It was eliminated from further testing.

**Table 4**

#### Immersion in Solution of Ammonium Salt of Aromatic Acids in Tap Water (0.75% wt)

Salt	Weight loss (mg)	% Protection (Z)
Ammonium salt of acid A	0.6	99%
Ammonium salt of acid B	0.5	99%
Ammonium salt of acid C	0.6	99%
Ammonium salt of acid D	24.6	45%
petroleum based VCI	0.6	99%
Tap water (control)	45	--

### Partial Immersion in Tap Water

Partial immersion in tap water containing 0.75% ammonium salt of A, of B, and of C, respectively, showed that these salts provided great protection in liquid phase, vapor phase, and liquid/vapor interphase, as illustrated in Figure 3, where the carbon steel panels experienced a 10 month partial immersion period. Ammonium salt of C produced a few corrosion spots on the edges in the areas of vapor phase and interphase. Ammonium salt of A, and of B, provided the same complete protection as the current petroleum-based VCI.





Salt of A                      Salt of C                      Salt of B                      Petro VCI  
**Figure 3: Partial Immersion in Solution of Ammonium Salt of Aromatic Acids In Tap Water (10months)**



**Immersion in Salt Water**

Individual ammonium salt of the tested aromatic acids provided modest protection for carbon steel immersed in salt water: ammonium salt of vanillic provided 38% protection, ammonium salt of ferulic 37%; while ammonium salt of cinnamic showed severe pitting, Table 5.

**Table 5**  
**Immersion of Carbon Steel in Solution of Ammonium Salt of var. Aromatic Acids in Salt Water**

Ammonium Salt of	%Salt (wt)	pH	Weight Loss (mg)	% Z	Carbon Steel after 10-day immersion
Acid A	0.75%	8.57	26	38%	
Acid C	0.75%	8.93	26	37%	



Acid B	0.75%	8.89	39	7%	
None (Control)	-----	7.14	42	--	

### Partial Immersion in Salt Water

Individual ammonium salt of the tested aromatic acids provided poor protection for carbon steel partially immersed in salt water: ammonium salt of acid A and ammonium salt of acid C showed heavy corrosion in vapor phase. Interestingly, ammonium salt of acid B showed protection that was slightly better than the protection by a conventional petroleum-based inhibitor, Table 6.

**Table 6**  
**Partial Immersion of Carbon Steel in Solution of Ammonium Salt of var. Aromatic Acids in Salt Water**

Ammonium Salt of	Amount of Ammonium Salt (% wt)	Partial Immersion Results
Acid A	1.9	Heavy corrosion in vapor phase
Acid C	2.1	Heavy corrosion in vapor phase
Acid B	2.2	Slightly better protection than a petro-based inhibitor
Petro-based Inhibitor	2.0	Nearly no corrosion on one side, but many streaks on the other side

### Corrosion Protection in Hydro Testing Using Salt Water

Though individual ammonium salt of acid A, of acid B, and of acid C, showed poor protection in salt water - in immersion test (Table 5) as well as in partial immersion test (Table 6), a combination (Combo) of them showed significant protection, Figure 4. The weight loss data confirmed that a combo of ammonium salts of B/C, and a combo of ammonium salts of B/A, both provided meaningful protection. The protection was 80% at combo salt concentration of 0.1%/0.1 for ammonium salt of B/ammonium salt of A; 92% at combo salt concentration of 0.25%/0.25% for ammonium salt of B/ammonium salt of C, Table 7. In some tests, an anionic surfactant was also added. It appears that the presence of the surfactant didn't play an important role, Table 7.



**Figure 4: 7 Days after Salty Hydro Testing Fluid Was Drained**

**Table 7  
Corrosion Protection in Hydro Testing Using Salt Water  
--With Additive of Combo Ammonium Salts of Aromatic Acids --**

Combo Type	conc %	% Protection
Ammonium salts of B/ C/ surfactant	0.5%/0.5%/0.15%	91%
	0.25%/0.25%/0.15%	92%
Ammonium salts of B/ A/ surfactant	0.5%/0.5%/0.05%	91%
	0.25%/0.25%/0.05%	89%
	0.1%/0.1%/0.05%	75%
Ammonium salts of B/ A (no surfactant)	0.5%/0.5%/0	90%
	0.25%/0.25%/0	85%
	0.1%/0.1%/0	80%

### CONCLUSIONS

Study on this selected group of commercially available biobased aromatic acids showed that an ammonium salt of these acids could be easily prepared. Ammonium salt of acid A and ammonium salt of acid C exhibited vapor inhibition ability (VIA), while ammonium salt of acid B and ammonium salt of acid D did not show this property.

Ammonium salt of A, of B, and of C, provided 99% protection in immersion test in tap water. Partial immersion in tap water for more than one year showed excellent protection in liquid phase, in vapor phase, and at liquid/vapor interphase was afforded by ammonium salt of A, and by ammonium salt of B. Ammonium salt of C also provided acceptable protection with minor corrosion spots on the edges in the areas of vapor phase and interphase.

When a combo of ammonium salts of B/A was used in a salt water hydro testing, a synergistic protection effect was shown. The protection reached 80% when the individual salt concentration was as low as 0.1%. A similar synergistic protection effect was also shown in a combo of ammonium salts of B/C.

Above findings points out that the biobased aromatic acids in this study are worthy candidates for a new generation of "green" corrosion inhibitors. Patents of the United States and other countries are pending on this work.

## REFERENCE

1. G2MT Laboratories, Cost of Corrosion Annually in the US Over \$1 Trillion, <http://www.g2mtlabs.com/cost-of-corrosion/>, viewed Sept. 15, 2014
2. NACE, Corrosion Costs and Preventative Strategies in the United States, <http://www.nace.org/uploadedFiles/Publications/ccsupp.pdf>, viewed Sept 15, 2014
3. James A.O. and Akaranta O., Inhibition of Corrosion of Zinc in Hydrochloric Acid Solution by Red Onion Skin Acetone Extract, *Res.J.chem.sci.*, 1(1), 31-37 (2011)
4. Akalezi, C.O, etc, Application of Aqueous Extracts of Coffee Senna for Control of Mild Steel Corrosion in Acidic Environments, *International Journal of Industrial Chemistry*, 3(13), 2012
5. Kavitha, N., Manjula P. and Anandha, K., Syneristic Effect of C. Papaya Leaves Extract-Zn<sup>2+</sup> in Corrosion Inhibition of Mild Steel in Aqueous Medium, *Research Journal of Chemical Sciences*, Vol. **4(8)**, 88-93, August (2014)
6. Sangeetha M., Rajendran S., Sathiyabama J. and P.Prabhakar P., Eco friendly extract of Banana peel as corrosion inhibitor for carbon steel in sea water, *J. Nat. Prod. Plant. Resour.*, 2(5), 601-610, (2012)
7. Hussin M.H. and Kassim M.J., Electro chemical studies of mild steel corrosion inhibition in aqueous solution by Uncariagambir extract, *Journal of Physical Science*, 2(1), 1-13, (2010)
8. Alinnor I.J., Ejikeme P.M., Corrosion inhibition of Aluminium in acidic medium by different extracts of *Ocimum gratissimum*, *American Chemical Science Journal*, 2(14), 122-135, (2012)
9. Lignoworks Research Network, What is Lignin? <http://www.lignoworks.ca/content/what-lignin>, viewed Sept 15, 2014
10. Akbarzadeh, E etc, Monomers of lignin as corrosion inhibitors for mild steel: study of their behaviour by factorial experimental design, *Corrosion Engineering, Science and Technology* ???
11. Quraishi. M, Development and testing of a Green Volatile Corrosion Inhibitor for Mild Steel, NACE, 2013
12. Bhagat, S.M., etc, Study of organic compounds containing - NH<sub>2</sub> and - COOH groups as corrosion inhibitor, *Oriental Journal of Chemistry*, Vol. 26(2), 649-653 (2010)

13. El-Etre. A.Y., Inhibition of acid corrosion of aluminum using vanillin, Corrosion Science, Volume 43, Issue 6, Pages 1031-1039
14. MIL-STD-3010, Department of defense test method standard: test procedures for packaging materials (30 Dec 2002)
15. ASTM G31, Standard Practice for Laboratory Immersion Corrosion Testing of Materials (2003)
16. ASTM G1, Standard Practice for Preparing, Cleaning, and Evaluation Corrosion Test Specimens (2003)