

Investigation of Bio-Based Aromatic Acids as Corrosion Inhibitors

MING SHEN, ALLA FURMAN, AND
RITA KHARSHAN, Cortec Corp., St. Paul,
Minnesota

Interest in corrosion mitigation utilizing renewable and biodegradable raw materials is quickly on the rise. Use of a number of plant materials as corrosion inhibitors has been reported; however, preparation of corrosion inhibitors from these source materials is often laborious, making industrial-scale application difficult. This work uses readily available bio-based materials; and aromatic acids, such as vanillic acid, ferulic acid, cinnamic acid, and mandelic acid, were studied as industrial corrosion inhibitors in vapor phase, various water-based electrolytes, and vapor/electrolyte interphase. Simple preparations demonstrated that some of these materials possess abilities as vapor phase corrosion inhibitors. Some preparations of the bio-based acids showed potential as additives for mild steel protection in immersion or partial immersion applications in water-based electrolytes. Synergistic combinations of different preparations showed superior performance over individual materials.

A recent estimate of the annual costs of corrosion in the United States is \$1 trillion,¹ more than three times the amount reported by NACE International in 2002.² That study found that ~\$121 billion per year was spent on methods to prevent and control corrosion, including \$0.4 billion spent on vapor corrosion inhibitors. New technologies derived from renewable, biodegradable,

and nonhazardous 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 byproducts will become economically advantageous.

A wide range of plant materials as corrosion inhibitors has been reported, from vegetables and fruits, such as red onions,³ coffee,⁴ papaya leaves,⁵ and banana peels,⁶ to many varieties of plant leaves.⁷⁻⁸ In many cases, however, the source materials are not commercially available; and the preparation of corrosion inhibitors from these source materials is laborious. The adoption of these types of green inhibitors is difficult on an industrial scale.

This work uses industrially available bio-based materials. In particular, a group of aromatic acids was studied as industrial corrosion inhibitors in vapor phase, various water-based electrolytes, and vapor/electrolyte interphase. These materials were chosen in part because they are derivatives of natural lignin, the second most abundant natural polymer in the world, surpassed only by cellulose.⁹ Table 1 summarizes the fundamental properties (molecular weight) of this group of acids from which the proprietary study compounds were derived.

Lignin derivatives have been reported to have corrosion-inhibiting properties. A literature search has indicated that ferulic acid protects mild steel in a near-neutral aqueous solution,¹⁰ cinnamic acid protects mild steel in a vapor phase¹¹ and acidic

medium,¹² and vanillic acid protects aluminum in an acidic solution.¹³

These bio-based aromatic acids were studied as salt compounds. Corrosion-inhibiting properties of the study compounds were compared with their petroleum-based counterparts. Interestingly, salts of Acids A and C exhibited volatile corrosion inhibition properties, while salts of Acids B and D did not. In addition, salts of Acids A, B, and C showed excellent protection of mild steel in partial immersion tests, making them worthy candidates as green inhibitors for the water treatment industry to easily meet discharge regulations. When salts of Acids A and B and Acids B and C were combined, a synergistic protective effect was found in hydrostatic testing using salt water.

Hydrostatic testing or hydrotesting 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 the testing liquid, corrosion protection of the vessels being tested, particularly those constructed of carbon steel (CS) or cast iron, must be considered. The protection challenge is greater when salty water is used due to the aggressive chloride electrolyte. Protection is needed when the vessel is filled with salty water and when the vessel is drained but remains exposed to salt residue, oxygen, and humidity.

Materials and Experimental Procedures

Preparing Salts of Aromatic Acids

Aromatic Acids A (97%), B (99%), C (99%), and D (99%) were purchased from Sigma Aldrich[†]. Each acid was made into a salt by reacting with an alkaline material in deionized water to a pH range from 9.5 to 10.5. Each solution contained 15% salt solid.

Metal Specimens

SAE 1010 (AISI 1010 [UNS G10100]) cold-rolled CS panels (1 by 4 in [25 by 102 mm]) were used in immersion tests and

partial immersion tests. AISI 1010 CS plugs (D = 15 mm, H = 13 mm) were used for vapor inhibiting ability (VIA) tests.

Evaluating Vapor Inhibiting Ability

VIA testing evaluates a product's ability to protect metal from corrosion without being in direct contact. The VIA test described here is based on Military Standard MIL-STD 3010B, Method 4031.¹⁴ An illustration of the VIA test assembly is shown in Figure 1(a). A test sample (in a dish of liquid or powder) is placed into a quart-size glass jar. The jar is capped with a lid that contains a freshly polished and cleaned CS plug (AISI 1010) for 20 h at an ambient temperature. A relative humidity of nearly 100% is then created in the jar (via the addition of 3% glycerol in water) for 2 h at an ambient temperature, followed by another 2 h at 40 °C.

After 24-h 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 the VIA grading chart in Figure 1(b)). The test is run in triplicate. The control is a plug exposed in a jar without an inhibitor (shown at the left of each group in Figure 1(b)).

TABLE 1. PROPERTIES OF THE ACIDS UPON WHICH THE PROPRIETARY STUDY COMPOUNDS WERE BASED

Name	MW	State
Acid A (vanillic)	168	White powder
Acid B (cinnamic)	148	White powder
Acid C (ferulic)	194	White powder
Acid D (mandelic)	152	White powder

Immersion and Partial Immersion Tests

The immersion and partial immersion tests were carried out per ASTM G31,¹⁵ either in tap water or in salty water (3.5% sodium chloride [NaCl]). The metal panels were cleaned per ASTM G1¹⁶ after testing.

The weight loss method was used to assess the corrosion protection (%Z) in the immersion test, as shown in Equation (1):

$$\%Z = 100 \times (C_c - C_i) / C_c \quad (1)$$

where C_c = weight loss without inhibitor and C_i = weight loss with corrosion inhibitor.

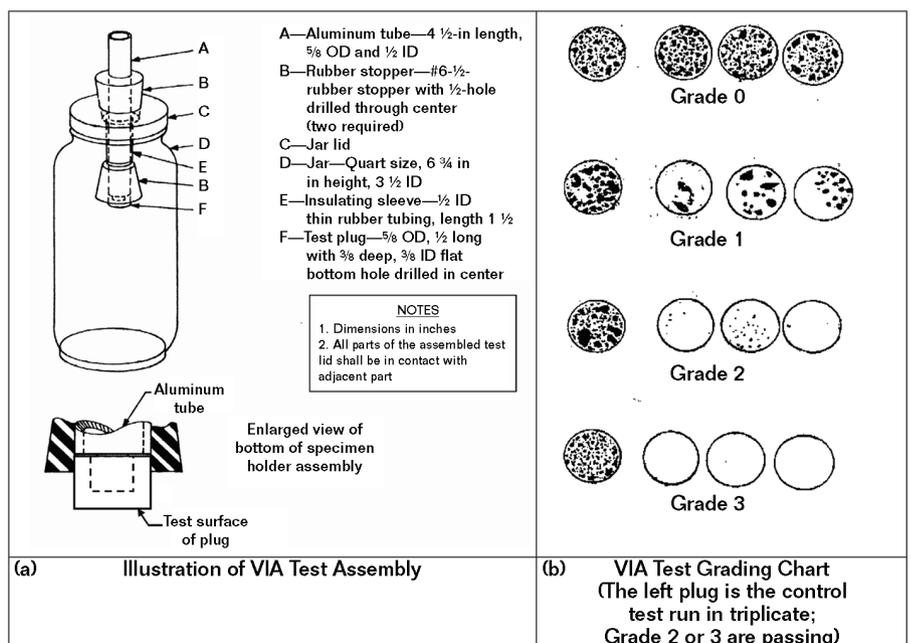


FIGURE 1 Illustration of VIA test.

[†]Trade name.



FIGURE 2 Setup of corrosion testing in a simulated hydrotesting environment.

lent to 0.15 g active salt) and acceptable at 0.5 g solution (0.075 g salt), shown in Table 2. Salts of cinnamic acid, however, did not show vapor protection ability.

When the salts of Acids A and C were applied to a piece of paper (2 by 5 in [51 by 127 mm]) and dried (10 min at 40 °C), the VIA test showed the paper also exhibited VIA, indicating that the salt solid possessed VIA (Table 3).

Immersion in Tap Water

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

Partial Immersion in Tap Water

Partial immersion in tap water containing 0.75 wt% salt of Acids A, B, and 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 CS panels were immersed for 10 months. The salt of Acid C produced a few corrosion spots on the edges in the areas of vapor phase and interphase. Salts of Acids A and B provided the same complete protection as the petroleum-based VCI.

Immersion in Salty Water

The individual salts of the tested aromatic acids provided modest protection for CS immersed in salty water: salt of vanillic acid provided 38% protection and salt of ferulic acid showed 37%; while salt of cinnamic acid showed severe pitting (Table 5).

Partial Immersion in Salty Water

Individual salts of the tested aromatic acids provided poor protection for CS partially immersed in salty water: the salt of Acid A and the salt of Acid C showed heavy corrosion in the vapor phase. In contrast, the salt of Acid B showed protection that was slightly better than the protection by a conventional petroleum-based inhibitor (Table 6).

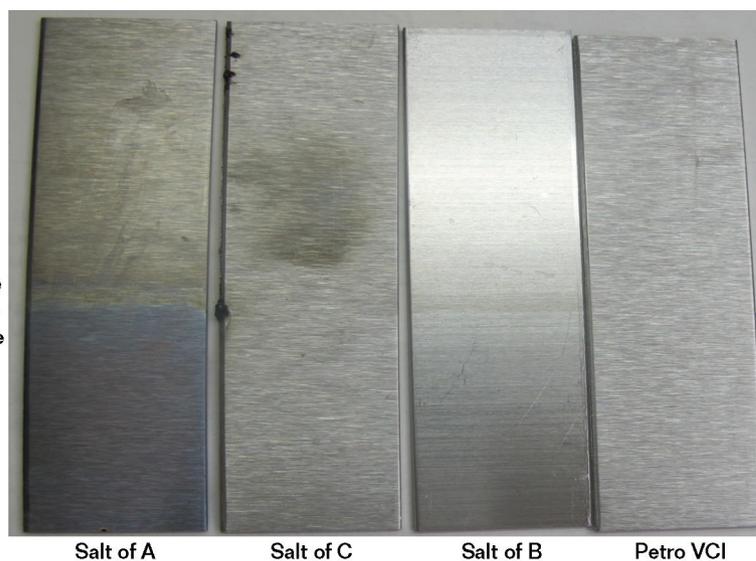


FIGURE 3 Partial immersion in tap water containing salt of an aromatic acid (10 months).

Hydrostatic Testing Corrosion

Corrosion of CS during and after hydrostatic testing using salty water was simulated in the laboratory setting by immersing an AISI 1010 CS panel in salty water (3.5% NaCl) in bottles, with and without an inhibitor additive, for 6 h, followed by draining off most of the testing liquid but keeping the steel panel in the capped bottle for seven 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 described in ASTM G1.

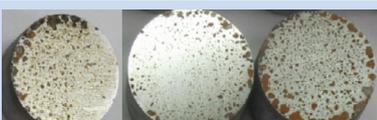
In addition to visual inspection and photographic recording, the weight loss method was used to assess the protection (%Z) in hydrostatic testing, as described in Equation (1).

Results

Vapor Inhibition Ability

The VIA test showed that salts of Acids A and C had VIA. Their vapor phase protection was excellent at 1 g solution (equiva-

TABLE 2. VIA TEST ON SOLUTION OF SALTS OF AROMATIC ACIDS

Specimen	Plugs	VIA Grade Pass/Fail
Salt of Acid A (1 g solution/0.15 g salt)		3,3,3 Pass
Salt of Acid C (1 g solution/0.15 g salt)		3,3,3 Pass
Salt of Acid B (1 g solution/0.15 g salt)		0,0,0 Fail
Salt of Acid D (1 g solution/0.15 g salt)		0,2,2 Fail
Salt of Acid A (0.5 g solution/0.075 g salt)		2,2,2 Pass
Salt of Acid C (0.5 g solution/0.075 g salt)		2,3,3 Pass
Control		0,0,0 Fail

Corrosion Protection after Hydrotesting Using Salty Water

Though individual salts of Acids A, B, and C showed poor protection in salty water in the immersion test (Table 5) and the partial immersion test (Table 6), a combination of salts showed significant protection (Figure 4). The weight loss data confirmed that a combination of salts of Acids B/C and the salts of Acids B/A both provided meaningful protection. The protection was 80% at a salt concentration of 0.1%/0.1% for salts of Acids B/A, and 92% at a combined salt concentration of 0.25%/

0.25% for salts of Acids B/C (Table 7). In some tests, an anionic surfactant was also added; however, it appears that the presence of the surfactant did not play an important role (Table 7).

Conclusions

The study of this selected group of commercially available bio-based aromatic acids shows that a salt of these acids could be prepared easily. Salts of Acids A and C exhibited VIA, while salts of Acids B and D did not show this property.

TABLE 3. VIA TEST ON 0.15 g DRIED SALT

Specimen	Test Plugs
Salt of A	
Salt of C	
Control	

Salts of Acids A, B, and C provided 99% protection in an immersion test in tap water. Partial immersion in tap water showed that excellent protection in the liquid phase, vapor phase, and at the liquid/vapor interphase was provided by salts of either Acids A or B. The protection is still excellent in the ongoing partial immersion test that is more than 30 months old. The salt of Acid C also provided acceptable protection with minor corrosion spots on the edges in the areas of vapor phase and interphase.

When a combination of salts of Acids B/A was used in salty water hydrotesting, 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 combination of salts of Acids B/C.

These findings point out that the bio-based aromatic acids in this study are worthy candidates for a new generation of green corrosion inhibitors. Patents in the United States and other countries are pending on this work.

References

- 1 G2MT Laboratories, "Cost of Corrosion Annually in the US Over \$1 Trillion," <http://www.g2mtlabs.com/cost-of-corrosion> (September 15, 2014).

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TABLE 4. IMMERSION IN TAP WATER CONTAINING SALT OF AROMATIC ACIDS (0.75 WT%)

Salt of Aromatic Acid	Weight Loss (mg)	% Protection (Z)
Salt of Acid A	0.6	99
Salt of Acid B	0.5	99
Salt of Acid C	0.6	99
Salt of Acid D	24.6	45
Petroleum-based VCI	0.6	99
Tap water (control)	45	—

- NACE International, "Corrosion Costs and Preventative Strategies in the United States, Cost of Corrosion Study Unveiled," 2002, <http://www.nace.org/uploadedFiles/Publications/ccsupp.pdf> (September 15, 2014).
- A.O. James, O. Akaranta, "Inhibition of Corrosion of Zinc in Hydrochloric Acid Solution by Red Onion Skin Acetone Extract," *Res. J. Chem. Sci.* 1, 1 (2011): pp. 31-37.
- C.O. Akalezi, et al., "Application of Aqueous Extracts of Coffee Senna for Control of Mild Steel Corrosion in Acidic Environments," *International J. of Industrial Chemistry* 3, 13 (2012).

TABLE 5. IMMERSION OF CS IN SALTY WATER CONTAINING OF SALT OF VARIOUS AROMATIC ACIDS

Salt of	Salt (wt%)	pH	Weight Loss (mg)	% Z	CS 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		

TABLE 6. PARTIAL IMMERSION OF CS IN SALTY WATER CONTAINING SALT OF VARIOUS AROMATIC ACIDS

Salt of	Amount of 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

- 5 N. Kavitha, et al., "Syneristic Effect of C. Papaya Leaves Extract-Zn²⁺ in Corrosion Inhibition of Mild Steel in Aqueous Medium," *Research J. of Chemical Sciences* 4, 8 (2014): pp. 88-93.
- 6 M. Sangeetha, et al., "Eco Friendly Extract of Banana Peel as Corrosion Inhibitor for Carbon Steel in Sea Water," *J. Nat. Prod. Plant. Resour.* 2, 5 (2012): pp. 601-610.
- 7 M.H. Hussin, M.J. Kassim, "Electrochemical Studies of Mild Steel Corrosion Inhibition in Aqueous Solution by Uncariagambir Extract," *J. Physical Science* 2, 1 (2010): pp. 1-13.
- 8 I.J. Alinnor, P.M. Ejikeme, "Corrosion Inhibition of Aluminium in Acidic Medium by Different Extracts of Ocimum Gratissimum," *American Chemical Science J.* 2, 14 (2012): pp. 122-135
- 9 Lignoworks NSERC CRSNG Research Network, "What is Lignin?" Western University Institute for Chemicals and Fuels from Alternative Resources, <http://www.lignoworks.ca/content/what-lignin> (September 15, 2014).
- 10 E. Akbarzadeh, et al., "Monomers of Lignin as Corrosion Inhibitors for Mild Steel: Study of Their Behaviour by Factorial Experimental Design," *Corrosion Engineering, Science and Technology* 47, 4 (2012): pp. 302-311.
- 11 M. Qurashi, "Development and Testing of a Green Volatile Corrosion Inhibitor for Mild Steel," CORROSION 2013, paper no. 02103 (Houston, TX: NACE International, 2013).
- 12 S.M. Bhagat, et al., "Study of Organic Compounds Containing -NH₂ and -COOH Groups as Corrosion Inhibitor," *Oriental J. of Chemistry* 26, 2 (2010): pp. 649-653
- 13 A.Y. El-Etre, "Inhibition of Acid Corrosion of Aluminum Using Vanillin," *Corros. Sci.* 43, 6 (2001): pp. 1,031-1,039.
- 14 MIL-STD-3010B, "Test Procedures for Packaging Materials" (Washington, DC: MIL, 2008).
- 15 ASTM G31, "Standard Practice for Laboratory Immersion Corrosion Testing of Materials" (West Conshohocken, PA: ASTM, 2003).
- 16 ASTM G1, "Standard Practice for Preparing, Cleaning, and Evaluation Corrosion Test Specimens" (West Conshohocken, PA: ASTM, 2003).

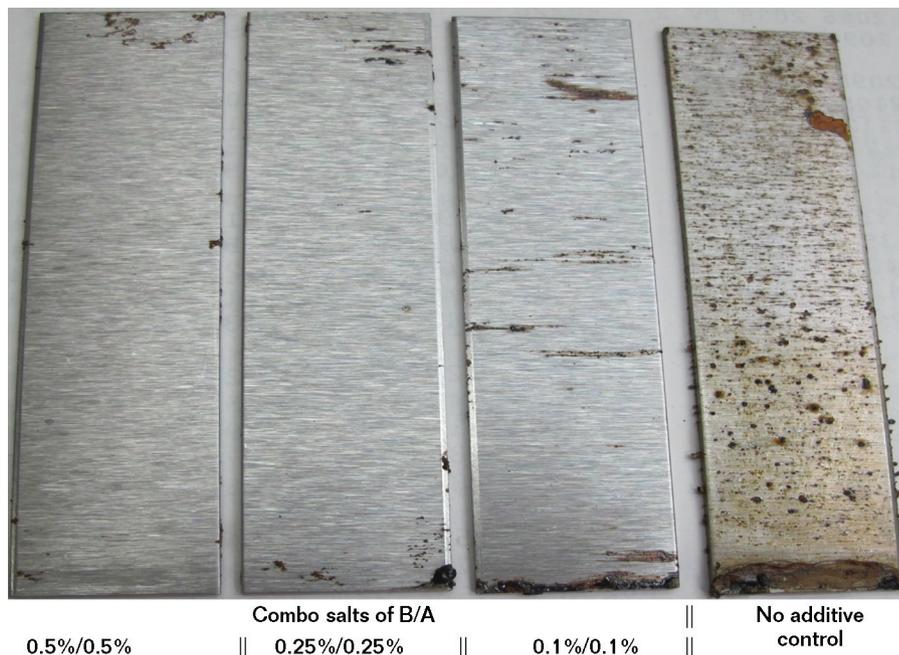


FIGURE 4 Seven days after salty hydrotesting fluid was drained.

TABLE 7. CORROSION PROTECTION IN HYDRO TESTING USING SALTY WATER—WITH ADDITIVE OF COMBO SALTS OF AROMATIC ACIDS

Combination Type	Concentration %	% Protection
Salts of B/C/surfactant	0.5/0.5/0.15	91
	0.25/0.25/0.15	92
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
Salts of B/A (no surfactant)	0.5/0.5/0	90
	0.25/0.25/0	85
	0.1/0.1/0	80

MING SHEN is the new product development manager at Cortec Corp., 4119 White Bear Pkwy., St. Paul, MN 55110, e-mail: mshen@cortecvci.com. She is involved in research and development of corrosion mitigation in the fields of water treatment, concrete, and oil and gas applications with an emphasis on environmentally friendly products. Her publications have appeared in MP, NACE annual conferences, EuroCorr, and LatinCorr. She has a Ph.D. in chemical engineering from the University of Virginia.

ALLA FURMAN, retired, was a senior corrosion engineer at Cortec Corp.

RITA KHARSHAN, retired, was the director of Cortec Laboratories, Inc. **MP**

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