Vapor Corrosion Inhibitors for Top-of-the-Line Corrosion

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Top-of-the-line corrosion in multiphase pipelines remains unsolved. Successful inhibitors should possess adequate volatility and strong affinity to the pipe metal in an acidic environment. Compounds were evaluated for protection of carbon steel at 70 °C with pH 4 condensates, with or without carbon dioxide (CO_2) flow. Azoles, certain acetylene alcohols, and a "green" volatile aldehyde were found to provide the best potential.

Top-of-the-line (TOL) corrosion typically occurs in wet gas pipelines that have a stratified flow regime and poor thermal insulation. They tend to contain high contents of carbon dioxide (CO_2) and organic acids (such as acetic acid [CH_3COOH] at 300 to 2,000 ppm in condensed water) and small amounts of hydrogen sulfide (H_2S). TOL corrosion is predominantly a problem of protection in the gas phase.[1] Some of the approaches to mitigate TOL corrosion include using corrosion-resistant alloys, applying protective layers to metal through pigging operations,[2-3] injecting corrosion inhibitors into the gas stream,[3] using innovative insulation materials for the pipelines, and changing the flow regime of produced gas.

Utilizing corrosion inhibitors is currently the most common method of corrosion protection in all petrochemical facilities, which spend, as an industry, $3.7 billion annually to mitigate corrosion.[4] Vapor corrosion inhibitors (VCIs), because of their ability to form a self-replenishing barrier layer, are important ingredients in the protection of pipelines, oil and gas wells, refinery units, fuels, and multiphase flow systems from a broad range of corrosive contaminants, such as humidity, condensation, oxygen, CO_2, and H_2S.[5-7]

In TOL systems, the inhibitors have to be effective in acidic conditions. This is especially challenging because commonly used amine-type VCIs react with acidic elements and lose their potency. TOL conditions require that successful corrosion inhibitors have the following characteristics:

- Effectiveness in the presence of organic acid
- Appreciable saturated vapor pressure
- Low potential of reaction with acidic environments

Cortec Corp. has developed a TOL corrosion inhibitor, Formula A, that achieved ~70% TOL protection in a corrosion loop test and 90% protection in the liquid contact phase (see "Results," p. 58). In order to strive for better protection, further screening of TOL corrosion inhibitors was conducted. The goal of this study was to evaluate a wide variety of candidates to find TOL corrosion inhibitors that are effective in acidic environments.

Three types of testing procedures were used—Corrosion Loop Test, Rotating Electrode Test, and Modified Vapor Inhibition Ability (VIA) Screening Test.

TABLE 1

Corrosion loop test parameters

Loop Parameters		Natural Gas Analysis	
Parameters	**Value**	**Component**	**mol%**
Test duration	8 h	H_2S	1.74
Gas type	Natural gas	Nitrogen	2.5
Gas volume	2.27 MMcm/d	Methane	69.4
Water content	240.6 Kg/MMcm	CO_2	1.42
Line size	508 mm ID, 12.2 m length	Ethane	12.0
Internal pressure	4.14 MPa	Propane	7.5
Internal temperature	350 °F (177 °C)	Iso-butane	1.0
Corrosive gas content	H_2S 1.74 mol%, CO_2 1.42 mol%, O_2 25 ppm	Butane	2.5
Inhibitor concentration	16.6 L/MMcm/d	Iso-pentance	0.5
Resistance coupon positions	12, 3, 6, and 9 o'clock	N-pentane	0.9
Corrosion rate measurement	Weight loss	Hexane	0.54

Experimental Procedure

Corrosion Loop Test

The test was conducted by an outside facility, Continental Products of Texas. See Table 1 for the corrosion loop test parameters.

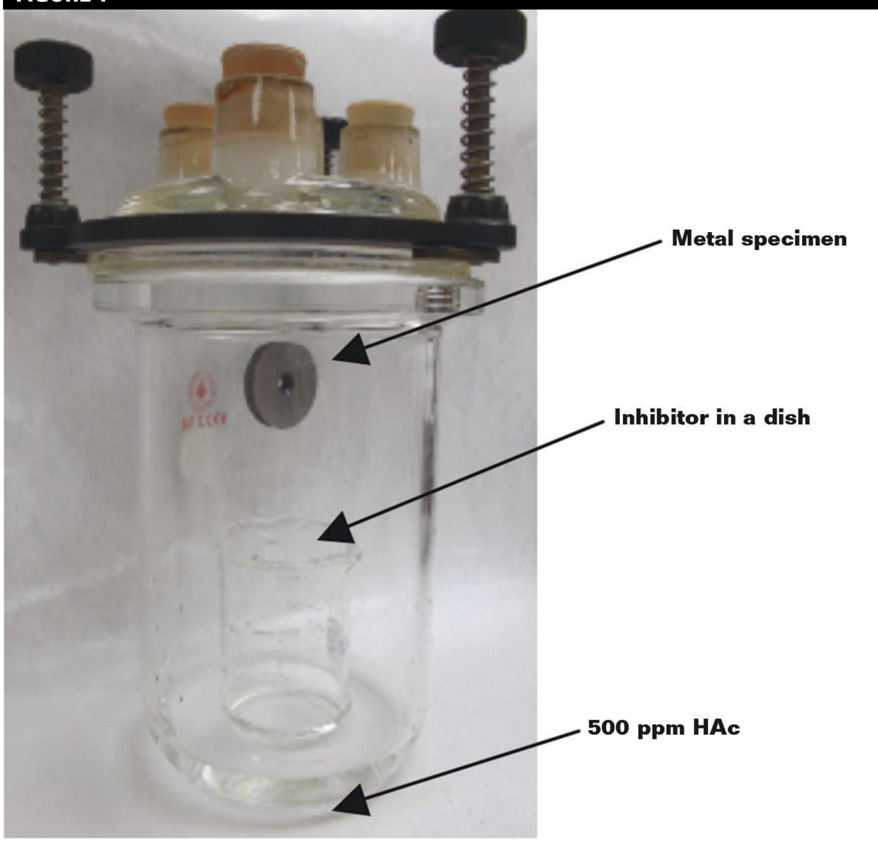
Rotating Cylinder Electrode Test

To conduct the rotating cylinder electrode test (ASTM G170-01[8]), an EG & G Versastate† potentiostat, with saturated calomel electrode as reference and high-density graphite as counter, was used. The working electrode was UNS G10180 (SAE-AISI 1018) carbon steel (CS) and the test electrolyte was 3.58% synthetic sea salt and 5% diesel fuel in deionized (DI) water. The test was performed at 150 °F (68 °C) with constant CO_2 bubbling (5×10^{-6} m^3/s). Linear polarization resistance (LPR) was measured at 1, 4, and 18 h after the addition of 50-ppm Formula A inhibitor.

Modified Vapor Inhibition Ability Test for Screening TOL Corrosion Inhibitor Candidates

The VIA test is based on the Federal Standard MIL-STD 3010B,[9] Method

FIGURE 1



Modified VIA test setup for an inhibitor in a dish.

†Trade name.

TABLE 2

Test results on Formula A

Loop Test Results (8 h, 177 °C)			
Coupon Position	**Corrosion Rate (mm/y) (Control)**	**Corrosion Rate (mm/y) (with Formula A)**	**% Improvement**
12 o'clock	1.42	0.41	71
3 o'clock	0.64	0.25	60
6 o'clock	0.31	0.03	92
9 o'clock	0.61	0.25	58

Rotating Cylinder Electrode Test Results						
Inhibitor	**Concentration (ppm)**	**Corrosion Rate (mm/y) without Inhibitor**	**Corrosion Rate with Inhibitor (mm/y) After 1 h**	**Corrosion Rate with Inhibitor (mm/y) After 4 h**	**Corrosion Rate with Inhibitor (mm/y) After 18 h**	**% Improvement Z[(A)]**
Formula A	50	1.673	0.068	0.044	0.027	98.3

[(A)]Z = 100 (Cc-Ci)/CC, where Cc is the corrosion rate in test electrolyte before inhibitor addition and Ci is the corrosion rate in test electrolyte 18 h after inhibition addition.

4031. Briefly, the method tests an inhibitor's protection in 100% relative humidity (RH), while not in direct contact, at 40 °C.

The modified VIA tests the protection of a TOL corrosion inhibitor in a vapor phase of 100% relative humidity that is ~pH 3.5, oxygen-free, and filled with CO_2 at 70 °C. A TOL corrosion inhibitor sample is placed in a 1-L glass vessel containing a 50-mL solution of 500-ppm acetic acid (HAc) in DI, pH 3.5. An inhibitor sample can be either in its own container (Figure 1), or mixed in a 500-ppm HAc solution.

An API 5L X65 steel coupon, freshly polished and cleaned, is hung inside the glass vessel by a fishing line. The vessel is purged with CO_2 (68.95 kPa, 8.3 × 10^{-6} m^3/s) for ~30 min to remove oxygen. The assembly is then placed in a 70 °C oven. The coupons are examined after 6 h.

A test would end if it was obvious that the compound under test was not effective; otherwise, the test would continue to 16 h. The protection of an inhibitor is determined by the appearance of the coupon compared with a control steel coupon that was exposed to the same testing conditions but without an inhibitor.

Results

A corrosion loop test showed that Formula A demonstrated 70% protection at the 12 o'clock position (TOL protection) and 92% protection at the 6 o'clock position (bottom-of-the-line [BOL] protection) at 177 °C in a natural gas stream that contained 240.6-kg water/MMcm gas, together with acid gas content of H_2S (1.74 mol%), CO_2 (1.42 mol%), and O_2 (25 ppm) (Table 2).

Rotating cylinder electrode test results showed that the 50-ppm Formula A provided 98% protection to CS in an electrolyte that contained 3.58% synthetic sea salt and 5% diesel fuel at 68 °C (Table 2). These data confirm the 6 o'clock position data (92% protection) from the corrosion loop test, indicating Formula A is an effective liquid phase inhibitor for gas pipelines.

Modified VIA screening tests were performed on a variety of selected compounds. Compounds not affected by acidic environments were particularly sought. Figure 2 presents a summary of the results. The results show that some azoles and acetylene alcohols provided TOL protection, while some other tested acetylene alcohols showed pitting. The tested sulfur-containing compounds also showed pitting. Blends of promising compounds were made into Formulas B and C for a possible synergetic effect and for elimination of localized corrosion.[10] They were evaluated in the modified VIA test along with Formula A. All showed promise for reducing TOL corrosion.

Conclusions

Among the evaluated substances, screening showed that the best potential for providing corrosion protection for TOL came from azoles, certain acetylene alcohols, and a "green" volatile aldehyde.

It was found that low molecular weight amines and derivates did not perform well, possibly because of their neutralization by acid environments.

Formula A provided 90% corrosion protection in the liquid phase and ~70% protection in the gas phase. It also provided better protection to UNS G10100 steel than to API 5L X65 steel. Further work will explore incorporating the promising TOL inhibitors with the existing formulas to provide better TOL corrosion protection.

Acknowledgments

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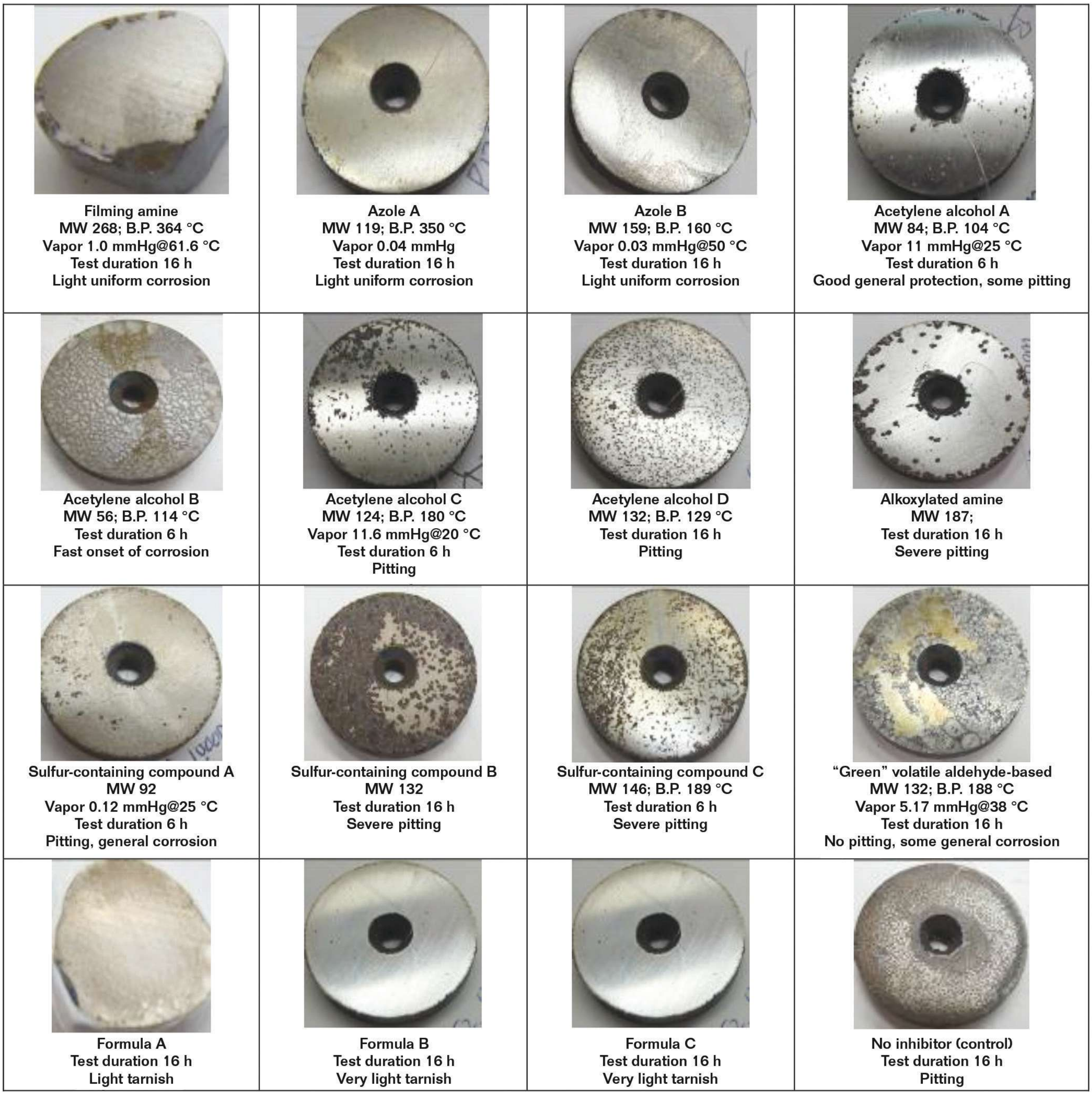
FIGURE 2



Results of modified VIA tests screening TOL corrosion inhibitors on API 5L X65 CS.

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