

Development of Corrosion Inhibitors for Prevention of Top of the Line Corrosion (TLC)

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ABSTRACT

Inhibition of Top of the Line Corrosion (TLC) in the multiphase natural gas pipelines remains unsolved in spite of numerous researches. The majority of studies in the area are still at the laboratory testing and screening phase. It is assumed that the effectiveness of the injected corrosion inhibitor strongly depends on its volatility. On the other hand, the harsh conditions of top of the line (TOL) application, including low pH of freshly condensed water and elevated temperature and pressure, require a strong affinity between the inhibitor molecule and the material of the pipe. A variety of compounds were selected based on their physical-chemical properties and the available data on the mechanisms of corrosion prevention. Testing includes the evaluation of corrosion inhibition of carbon steel at 70 °C with pH4 condensate, with and without the flow of carbon dioxide. It was found that azoles, certain acetylene alcohol, and a "green" volatile aldehyde provided the best potential for TLC prevention.

Key words: Inhibitor, corrosion protection, top of the line, natural gas pipeline, corrosion rate.

INTRODUCTION

In today's industrial world cost saving is of paramount importance. There is a continuous search for new and innovative solutions that extend the working life of existing assets and infrastructure while lowering environmental impact. The world of pipelines is no different in its search for smarter and greener solutions. As a large number of gas transport pipelines continue to mature, and maintenance and operating costs continue to rise, there has been an increased focus on finding environmentally friendly, innovative solutions to achieve these goals.

Top of line corrosion (TLC) occurs when, in multiphase flow, acidic water vapor condenses at the top and side of the pipeline, leading to severe corrosion attacks that are difficult to mitigate¹. TLC occurs typically in wet gas pipelines with stratified flow regime that are poorly

insulated thermally. They tend to contain high contents of CO₂ and organic acids (such as acetic acid at 300-2000ppm in condensed water) and small amounts of H₂S. TLC is predominantly a problem of protection in the gas phase¹. A complex approach is required to eliminate/reduce TLC.

Some of the approaches include using corrosion resistant alloys, applying protective layers to metal through pigging operations^{2,3}, injecting corrosion inhibitors to the gas stream³, using innovative insulation materials for the pipelines, and changing flow regime of produced gas

Utilizing corrosion inhibitors is currently the most common method of protection against corrosion in all petrochemical facilities. Based on the latest information, the oil and gas industry spends \$3.7 billion per year to mitigate corrosion⁴

Vapor corrosion inhibitor (VCI) products provide a very high level of protection for steel from a broad range of corrosive contaminants, such as moisture, condensation, oxygen, carbon dioxide, and hydrogen sulfide. With their ability to form self-replenishing barrier layer, VCIs are important ingredients in the protection of pipelines, oil and gas wells, refinery units, fuels, and multiphase flow systems^{5,6,7}.

In the case of TLC, the inhibitors have to be effective in acidic conditions due to the presence of organic (acetic) acids and trace amount of H₂S in the gas stream. This is especially challenging for commonly used amine-type VCIs because of chemical reactions between amine and acidic elements that result in reduced inhibition properties.

The conditions of TOL require that successful corrosion inhibitors have the following characteristics:

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

Cortec^(†) has developed a TOL inhibitor, Formula A, that achieved approximately 70% TOL protection in a corrosion loop test and 90% protection in the liquid contact phase (data below). In order to strive for better protection, further screening for TOL inhibitors was conducted.

The goal of this study is to evaluate a wide variety of TOL inhibitor candidates to find TOL inhibitors that are effective in acidic environments.

Four types of testing procedures were used in this study:

- Corrosion Loop Test
- Rotating Electrode Test
- Small Scale Corrosion Test
- Modified VIA Screening Test

EXPERIMENTAL PROCEDURE

[†] Trade name

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Corrosion Loop Test

The test was conducted by an outside facility, Continental Products of Texas^(§).

Table 1
Corrosion Loop Test Parameters

Parameters	Value
Test duration	8 h
Gas type	Natural gas
Gas volume	2.27MMcm per day
Water content	240.6Kg per MMcm
Line size	5.08cm ID, 12.2m length
Internal pressure	4.14 MPa
Internal temperature	350F/177°C
Acid gas content	H ₂ S 1.74 mol%, CO ₂ 1.42 mol%, O ₂ 25ppm
Inhibitor concentration	16.6L per MMcm per day
Resistance coupon positions	12:00, 3:00, 6:00 and 9:00 o'clock
Corr. rate measurement	Weight loss

Table 2
Natural Gas Analysis

<u>COMPONENT</u>	<u>MOLE %</u>
1) Hydrogen sulfide	1.74
2) Nitrogen	2.5
3) Methane	69.4
4) Carbon dioxide	1.42
5) Ethane	12.0
6) Propane	7.5
7) Iso-Butane	1.0
8) Butane	2.5
9) Iso-Pentane	0.5
10) N-Pentane	0.9
11) Hexane +	<u>0.54</u>
TOTALS	100.0

Rotating Cylinder Electrode Test

The test is per ASTM^(*) G 170-01: Standard Guide for Evaluating and Qualifying Oilfield and Refinery Corrosion Inhibitors in the Laboratory⁸.

Table 3
Rotating Cylinder Electrode Test Conditions

Parameters	Value
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[§] Trade name

^{*} ASTM International, 100 Barr Harbor Dr., PO Box C700, West Conshohocken, PA, 19428

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Potentiostat	'Versastate' [♦] (EG & G)
Reference electrode	Saturated Calomel Electrode
Counter electrode	High Density Graphite
Working electrode	G10180 (SAE1018)
Test electrolyte	3.58% Synthetic sea salt and 5% diesel fuel in DI water
Temperature	150°F/68°C
Purging gas	CO ₂ @5x10 ⁻⁶ (m ³ /s)
Inhibitor, concentration	Formula A @ 50ppm
Corr. rate measurement	LPR, at 1, 4 and 18 h after inhibitor addition

Small Scale Corrosion Study

Small scale corrosion study tests the protection of an inhibitor for a metal probe that experiences temperature differentials across its top and bottom surfaces. Figure 1 illustrates the test setting. 750mL of 500ppm acetic acid (HAc) solution, with and without inhibitor sample, is placed in a 1L glass vessel. The pH of the solution is recorded. A freshly polished and cleaned metal probe, either an ER probe (Microcor Online Corrosion Monitoring System, Rohrback Cosasco Systems) or a metal plug, is installed to the glass vessel lid. The plug is held by a hollowed-out rubber stopper so that the bottom of the plug is exposed to heated acidic humidity while the top of the plug is exposed to room temperature to allow condensation on the plug. Liquid and vapor temperatures inside the glass vessel are monitored. A condenser is used to allow the vapor to be cooled down and the condensate to drip back to the glass vessel. The assembled system is closed and purged with CO₂ (68.95kPa, 8.3x10⁻⁶ m³/s) continuously throughout the test duration. Heating starts after about 40 minutes of CO₂ purging when oxygen in the system has been eliminated. The temperature in vapor phase is kept at 70°C. At the end of the test, the pH of the condensate on the vessel's lid or sides is measured with a pH strip. The corrosion rate is measured using weight loss probes, electrical resistance techniques or by visual evaluation of the metal surface.

[♦] Trade name

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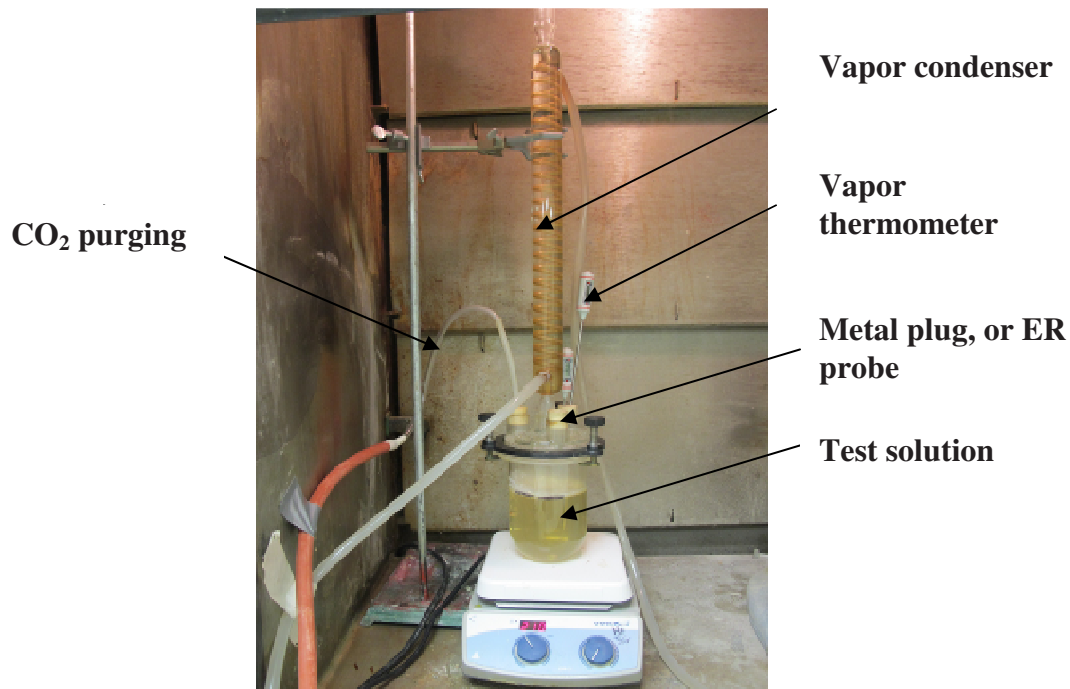


Figure 1 Illustration of Small Scale Corrosion Test

Table 4
Small Scale Corrosion Test Conditions

Parameters	Value
Temperature in gas phase	70 °C
Blank solution	750 ml 500ppm HAc in DI water
pH of blank solution	3.5
Purging gas	CO ₂ @68.95kPa, 8.3x10 ⁻⁶ m ³ /s
Metal	G10100(SAE1010) Steel , X65 [♦] pipe steel
Inhibitor amount	various
Test duration	various
Corr. Rate measurement	ER; weight loss; visual assessment

Modified Vapor Inhibition Ability (VIA) Test for Screening TOL Candidates

VIA test is a test of protection without being in direct contact. VIA test is based on the Federal Standard MIL-STD 3010B, Method 4031⁹. Briefly, an inhibitor's protection in 100% relative humidity is tested at 40 °C.

The modified VIA test for TOL product tests protection of a TOL inhibitor in a vapor phase with 100% relative humidity and a pH of approximately 3.5 that is oxygen-free and filled with CO₂ at 70 °C. Specifically, a TOL inhibitor sample is placed in a 1L glass vessel that contains 50ml solution of 500ppm acetic acid (HAc) in DI, pH 3.5 (blank solution). An inhibitor sample can be either in its own container (Figure 2-1), or mixed in the blank solution (Figure 2-2). A steel coupon, freshly polished and cleaned, is hung inside the glass vessel through a fishing line

[♦] X65 steel is low-carbon steel used primarily in the oil and gas pipelines. It is per American Petroleum Institute (API) standard.

that is attached to a rubber stopper. The vessel is purged with CO₂ (68.95kPa, 8.3x10⁻⁶ m³/s) for approximately 30 min to remove oxygen. The assembly is then placed in a 70 °C oven. The coupon is examined periodically for signs of corrosion. The protection afforded by an inhibitor sample is determined by its appearance with a control: a steel coupon exposed to the same testing conditions but without an inhibitor. Figure 2 illustrates this test setting.

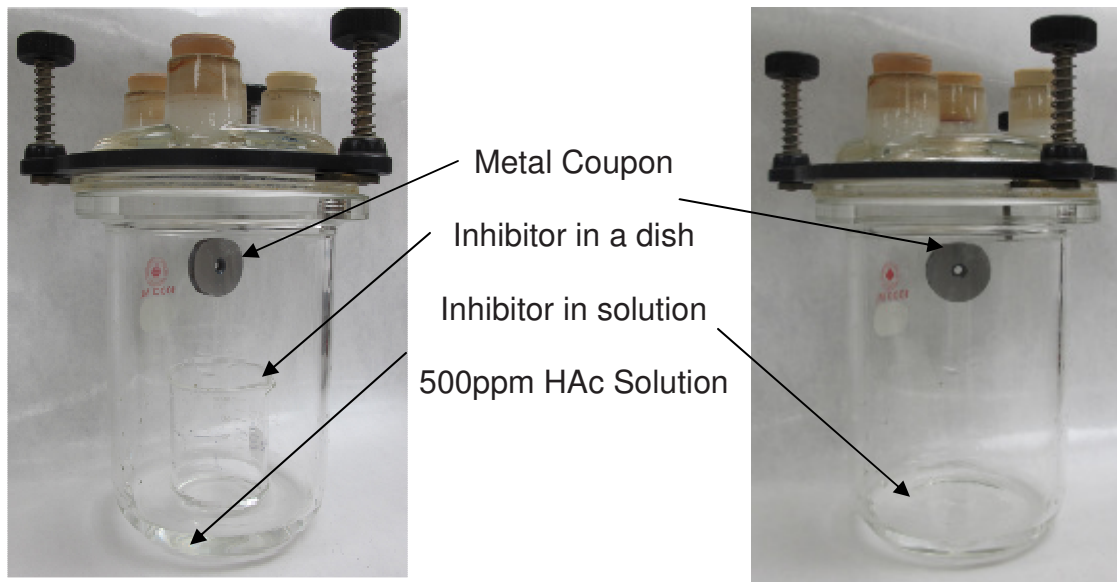


Figure 2-1, Modified VIA Test- Inhibitor in a dish

Figure 2-2. Modified VIA Test- Inhibitor in solution

Table 5
Modified VIA Test Conditions

Parameters	Value
Temperature	70 °C
Blank solution	50 ml 500ppm HAc in DI water
pH of blank solution	3.5
Purging gas	CO ₂ , 30 min
Metal	X65 pipe steel
Inhibitor amount	1.2 g, or Var. concentrations
Test duration	various

RESULTS

1. TOL protection of Formula A was tested in a corrosion loop test. The results show that at 177 °C, in natural gas stream that contained 240.6Kg water per MMcm gas, together with acid gas content of H₂S (1.74 mol%), CO₂ (1.42 mol%) and O₂ (25ppm), Formula A demonstrated 70% protection at 12:00 o'clock position and 92% protection at 6:00 o'clock position (Table 6). This data indicated that Formula A provided 70% TOL protection and 92% BOL protection.

Table 6
Corrosion Loop Test Results for Formula A
- At the End of 8h Testing -

Coupon position	Corr Rate (mm/yr) -Control-	Corr Rate (mm/yr) - with Formula A-	% Improvement
12:00 o'clock	1.42	0.41	71%
3:00 o'clock	0.64	0.25	60%
6:00 o'clock	0.31	0.03	92%
9:00 o'clock	0.61	0.25	58%

2. Rotating Cylinder Electrode Test results showed that the 50ppm Formula A provided 98% protection to carbon steel in an electrolyte that contained 3.58% synthetic sea salt and 5% diesel fuel at 68 °C (Table 7). This data confirms the 6:00 o'clock position data (92% protection) from the corrosion loop test, indicating Formula A is an effective liquid phase inhibitor for gas pipelines.

Table 7 Rotating Cylinder Electrode Test Results

Inhibitor	Conc ppm	Corr. Rate (mm/y) w/o inhibitor	Corr. Rate w/ inhibitor (mm/y) after 1 h	Corr. rate w/ inhibitor (mm/y) after 4 h	Corr. rate w/ inhibitor (mm/y) after 18 hours	% improv Z*
Formula A	50	1.673	0.068	0.044	0.027	98.3

*Z= 100 (Cc-Ci)/Cc, where

Cc – corrosion rate in test electrolyte before inhibitor addition

Ci – corrosion rate in test electrolyte 18 hrs after inhibitor addition


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3. Small Scale Corrosion Test was conducted for Formula A on G10100 steel and X65 pipe steel. The resulting plug at the end of the test was compared, by visual appearance, with a control plug exposed to the similar test conditions but without inhibitor. The results show that 0.1% Formula A provided good protection to SAE1010 steel, but no protection to X65 steel (Table 8).

Table 8
Results of Small Scale Corrosion Study on Formula A

Formula	Metal	Conc.	Test duration	Coupon -w/o inhibitor -control	Coupon -w/ inhibitor	Note	pH -Initial liquid	pH-condensate
Formula A	G10100	0.1%	47 h			Slight tarnish only. Good inhibition	3.7	~4
Formula A	X65	0.1%	47 h			Not good inhibition	3.7	~4

Small scale corrosion test was also conducted on a 1:1 blend of Dicyclohexylamine (DCHA) and oleylamine (OA) in both the liquid and vapor phases, using an ER probe. The results show that this blend of DCHA and OA provide effective corrosion protection in pH 4 solution (Figure 3) but not in its condensate (Figure 4).

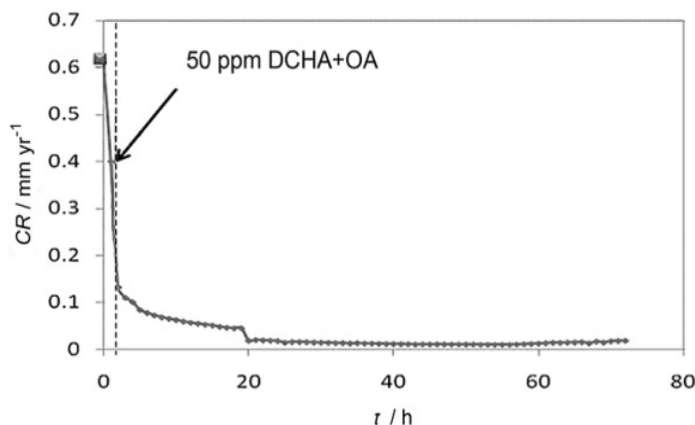


Figure 3: Corrosion rate of mild steel in solution of 3 wt % NaCl at 20°C, pH 4, without and with 50 ppm DCHA+OA measured with LPR during 72 h

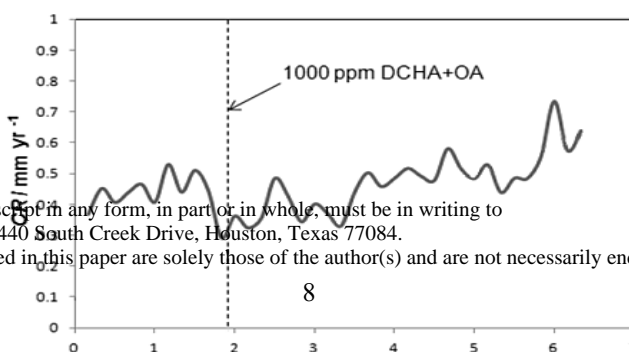



Figure 4: Corrosion rate of mild steel in vapor phase when 1000 ppm DCHA+OA was added in 3 wt % NaCl solution at 70°C, pH 4 with 1000 ppm of acetic acid

4. Modified VIA screening tests were performed on a variety of selected compounds. Compounds that will not be affected by acidic environments were particularly sought after. Coupons were examined after 6 h of testing. If it became obvious that the testing compound was not an effective inhibitor, testing was ended; otherwise, the testing would be allowed to continue to 16 hours. A summary of the results are presented in Table 9. The corrosion of a coupon at the end of test was compared, by visual appearance, with that of a control coupon under similar test conditions but without inhibitor. The results show that some azoles and some acetylene alcohol 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 the possibility of synergetic effect and for elimination of localized corrosion¹⁰. They, along with Formula A, were evaluated in modified VIA test. All showed promising reduction in TOL corrosion.

**Table 9
Results of Modified VIA Test - Screening for TOL Inhibitor –X65 Carbon Steel**









Inhibitor	FW	Boil pt (°C)	Vapor pressure	Amount of inhibitor	Test duration	Coupon-w/o inhibitor -Control-	Coupon –with inhibitor	Note
Filming Amine	268	364	1.0 mmHg @61.6 C	1.2 g in a dish	16 h			Light uniform corrosion
Azole A	119	350	0.04 mmHg @20 °C	4000ppm in solution	16 h			Light uniform corrosion
Azole B	159	160	0.03 mmHg @50 C	4000ppm	16 h			Light uniform corrosion

Acetylene alcohol A	84	104	11 mmHg @25C	2000ppm	6 h			Good general inhibition; some pitting
Acetylene alcohol B	56	114		1.2g	6 h			Fast onset of corrosion
Acetylene alcohol C	124	180	11.6 mmHg @20 °C	1.2g	6 h			pitting
Acetylene alcohol D	132	129		1.2g	6 h			pitting
Alkoxylated amine	187			1000ppm	16 h			Sever Pitting
Sulfur Containing Compound A	92		0.12 mmHg @25C	1000ppm	6 h			Pitting; general corrosion
Sulfur Containing Compound B	132			5000ppm	16 h			Severe pitting
Sulfur Containing Compound C	146	189		1%	6 h			Pitting

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"green" volatile aldehyde based	132	188	5.17 mmHg @38C	1%	16 h			Moderate Corrosion, no pitting
Formula A				1.2g	16 h			Light tarnish only
Formula B				0.5%	16 h			Very light uniform corrosion, few pitting
Formula C				0.5%	16 h			Very light uniform corrosion

CONCLUSIONS

1. Formula A provided 90% corrosion protection in liquid phase, but only provided ~70% protection in gas phase. It also provided better protection to G10100 steel than to X65 steel.
2. Small Scale Corrosion Test on a blend of amine (1:1 DCHA:OA) show that this blend of amine is not an effective inhibitor in condensate in an acidic environment, most likely due to neutralization. As such, search of TOL inhibitors needs to expand beyond the amine family.
3. The modified VIA test screening showed that among the evaluated substances the best potential for providing corrosion protection for TOL came from azoles, certain acetylene alcohol and a 'green' volatile aldehyde. These compounds show promise as TOL inhibitors partly because they do not tend to be "consumed" by the acidic environment common in TOL situations.
4. From modified VIA test, filming amine was found to be not as effective as azoles and certain acetylene alcohols at the comparable concentration level, most likely due to its low volatility. At the same time low molecular weight amines and derivatives did not perform well, possibly because of their neutralization by acid environments.
5. Further work will involve exploring incorporating the promising TOL inhibitors with the existing formulas to provide better TOL protection.

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