# INCORPORATING VAPOR CORROSION INHIBITORS (VCIS) IN OIL AND GAS PIPELINE ADDITIVE FORMULATIONS

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## ABSTRACT

Two new oil and gas pipeline additives were formulated utilizing volatile corrosion inhibitors (VCIs).  These products provide a very high level of protection for steel subjected to different types of corrosive petrochemicals due to surface adsorption and vapor phase action environments.

The formulation work was based on fatty acid imidazoline chemistry combined with different organic acids. Different surfactants were used to provide maximum wetting properties to the inhibitor and faster transport of inhibitor from the oil or gas phase to the water.  Vapor corrosion inhibitors were introduced in the formulation.  A Windows-compatible software was used to identify the vital factors that affect the quality of the product.

The protective properties of newly developed inhibitors were evaluated in various types of corrosive mediums.

Keywords:  vapor corrosion inhibitors (VCIs), oil and gas pipeline additives, imidazoline, fatty acids, "wheel" corrosion test, electrochemical techniques, continuous treatment, film persistency, steel, organic acids, surfactants, petrochemical, SCC (stress corrosion cracking).

## INTRODUCTION

Corrosion of pipes, pumps, turbine blades, coolers, superheaters, reheaters, fuel cells and exhaust systems causes enormous industrial expenses due to production downtime, accidental injuries and replacement cost.  According to Zenneti [1], the cost to the United States industry from corrosion exceeds $10 billion per year.  The market for corrosion inhibitors in the United States is expected to increase to $7.1 billion per year by the year 2000 [2].  In the last few years a number of new oil and gas fields were discovered in different regions of the world.  Several common features of these newly discovered deposits are:  a high level of water encroachment (reaching 80%), high concentration of $H_2S$, $CO_2$ and $O_2$, and a high level of brine mineralization, to name just a few.  All of these factors cause damage to equipment and catastrophic failures of pipelines.

Utilization of corrosion inhibitors is currently the major way of protecting against corrosion in all petrochemical facilities in the world. Some of the most effective corrosion inhibitors for oil and gas pipeline application are the fatty acid imidazoline type of products. However, imidazolines have very low solubility in a water phase and to increase solubility, these compounds are usually used in conjunction with acids. The most common acid of these types of formulations is acetic acid, which does not give any additional protection [3].

The purpose of this work is to determine the effectiveness of two new VCIs to be used in oil and gas pipelines, formulations which are based on fatty acid imidazolines, special classes of organic acids, active wetting agents and vapor corrosion inhibitors. This work is a continuation of a study for using vapor corrosion inhibitors in the petrochemical industry [4].

## EXPERIMENTAL MATERIALS

Panels: SAE CS1010

Fatty Acid Imidazoline

The fatty acid imidazoline consists of the following: an imidazoline, a long hydrocarbon tail group and a short pendent group (Figure 1). According to Ramachandan [5] the best corrosion protection is provided by imidazolines containing ethylamino group as a pendent group and fatty acid radical (hydrocarbon tail) containing not lower than $C_{15}$. This kind of imidazoline was used in our work and will be further named as a fatty acid imidazoline (FAI).

Organic Acids

The long chain organic acids were chosen for a new formulation based on our knowledge of their film-forming properties: Dimer acid (DA) and tall oil fatty acid anhydride (TOFAA). Acetic acid (AA) was used for comparison testing.

Surfactants

A long chain linear ethoxylated alcohol, sorbitan monooleate and aromatic sulfonates were used as surfactants (Surf).

Vapor Phase Inhibitors

Aminocarboxylates (AC) were used in the formulation to provide protection in the vapor phase.

Solvents

Different blends of co-solvents were used to provide stability of the final formulation:

Water - Isopropanol for the formulation containing DA
Mineral spirits - Isopropanol for the formulation containing TOFAA.

## PROCEDURE

A two-level, factorial experimental design was used to choose the best ratio and to study the input of each component and their combination on the quality of the product. Design Ease Software, version 3.0.8, Stat-Ease, Inc., was used to set up the experiment and helped to analyze the data. Two parameters were checked for each sample: compatibility and protective ability.

Compatibility

Compatibility was evaluated visually and results were rated using a scale of 1 to 10. A rating of 10 is for the samples which are compatible and did not give separation and/or precipitation, and the lower ratings are for the samples which were not compatible or were cloudy (turbid).

Protection

The protective ability was evaluated using a static immersion test. 200 ppm of the inhibitor was added to a solution containing 5% NaCl + 0.5% $CH_3COOH$ + 500 ppm $H_2S$ in deionized water. The carbon steel SAE 1010 panels were washed with methanol, weighed using an analytical scale and were immersed in the above mentioned solution. The solution without inhibitors was used as a control. The weight loss of the panels was determined after 24 hours at 50ºC while immersed in the solution.

The corrosion products were removed by dipping the panels in a rust remover for 1 minute followed with rinsing in tap water and drying. The protective power (Z) was calculated and rated using a scale of 1 to 10, where 10 represented highest protection and 1, the least protection (see Tables 1, 2, 3).

Based on empirical results, several formulations were prepared using different kinds and amounts of amines, fatty acids, surfactants and solvents. The protective ability for these samples was evaluated using the static immersion test (mentioned above).

The samples which showed the best protection in a static immersion test were then tested in a sweet ($CO_2$ present) dynamic immersion test. The carbon steel panels were prepared as described above. The panels were subjected to the sweet dynamic immersion test for 48 hours keeping the solution stirred at a rate of 200 rotations/minute. Results are presented in Table 3.

Polarization curves using the Tafel technique were obtained using the Potentiastat/Galvanostat "Versastat" from EG&G Company with corrosion software SoftCorr™ 252/352 in a 5% NaCl + 0.5% $CH_3COOH$ solution with the following electrodes:

| | |
|---|---|
| Working: | Carbon steel SAE 1010 |
| Reference: | Saturated calomel electrode (SCE) |
| Counter: | High density graphite electrode |

The tests were conducted at ambient temperature and by aeration. A one liter flask with a flat bottom was used as a corrosion cell. The working electrode was mounted by the leak-proof assembly at the center of it. The reference electrode was incorporated through the ultra-low leakage bridge table next to the working electrode.

Two high-density graphite counter electrodes were placed symmetrically from each side of the working electrode.

Two types of experiments were performed.

1. The inhibitor was added to the electrolyte at a concentration level of 200 ppm.
2. Before the polarization curves were taken, the working electrode was dipped in inhibitor and was air-dried.

The results are presented in Table 4 and in Figures 2 and 3.

"Wheel" Test (according to NACE test publication ID182). This test was performed for both film persistency and continuous treatment conditions (see Tables 5, 6).

A mixture containing 90% of electrolyte (9.62% NaCl + 0.305% $CaCl_2$ + 0.186% $MgCl_2$ x $6H_2O$ + 500 ppm $H_2S$ saturated with $CO_2$) and 10% of depolarized kerosene was used as a corrosion medium. Coupons were prepared from sandblasted mild steel skimstock. The test was performed at 150ºF (66ºC). The effectiveness of the inhibitors was evaluated by weight loss measurements.

Film Persistency Test. This test consisted of three steps:

1. Coupons were placed in capped bottles containing the above mentioned but inhibited mixture and were rotated in the wheel for a duration of 1 hour at 150ºF (66ºC) to enable the coupons to be "filmed" by the inhibited fluid.

2.    The coupons were than removed from the bottles, transferred to another bottle with the above mentioned mixer without inhibitor and rotated for another hour to rinse off loose inhibitor clinging to the coupon.

3.    The coupons were transferred to another bottle and exposed to the rotation in the mixture with no inhibitor for 24 hours.

Continuous Treatment Procedure.  The procedure was as follows: the coupons were exposed to the same corrosive media containing the inhibitor in the above mentioned conditions for 24 hours.

The concentration level of the inhibitors are stated in Tables 5 and 6.

Vapor Inhibition Ability Test.  The effectiveness of the inhibitors in the vapor phase were evaluated.  The samples in a 1% concentration of inhibitor were prepared for this evaluation:

#1 + Xylene
#4 + Xylene
Control (Xylene)

Xylene was used as the oil phase, because according to Pfeiffer [7], it represents the low boiling fraction of crude oil.  The three samples mentioned above were placed in three different 1-liter jars.  A beaker with 20 mL of water was placed in each jar and carbon steel panels (one panel per jar) were attached to the lids of the jars.  The products were subjected to the following cycling:  16 hours at 40ºC and 8 hours at room temperature.  The panels were inspected daily for any sign of corrosion.  The results are shown in Table 7.

Stress Corrosion Cracking (SCC).  The ability of the inhibitors to reduce the stress corrosion cracking was studied using the Cortest "Proof Ring" and tension specimen from steel ANSI 1045-1018, annealed, diameter 0.25 inch under the load 4,000 pounds in a solution 5% NaCl + 0.05% $CH_3CO_2H$, saturated with $H_2S$ for 20 minutes (NACE standard TM-01-77).  The time before cracking occurred was used as criteria to rate samples (Table 8).

RESULTS AND DISCUSSION

Using the experimental design procedure, 8 different samples were prepared (Table 1) based on a FAI and AA as a standard.

The data in Table 1 was analyzed and looking at DSN ID #5 and #8 (under column labeled Std.), one can see they performed the best (performance is calculated by adding the two performance scores from the Corr. test and the Comp. test; they both received a 16).  The Design Ease® software showed that compatibility depends mostly on the solvent content (Table 2), while the protective ability depends on the FAI content.

Based on the performance data obtained from the experimental design, three samples were prepared and tested using a ratio of FAI; acid; and surfactant very close to the one shown in Table 1.

Sample 1:        FAI + DA + Surf. + VCI + Solvent
Sample 2:        FAI + TOFAA + Surf. + VCI + Solvent
Sample 3:        FAI + AA + Surf. + VCI + Solvent
Sample 4*:       FAI + AA + Quaternary amine + Solvent

*Sample #4 is the formulation of a currently used standard corrosion inhibitor package used in industry.

Results given in Table 3 show that carboxylic acid strongly affects the ability of protection of this inhibitor formulation.  The protection of formulations containing long chain organic acids are much higher than the same containing AA.

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The presence of a surfactant helps to provide better wetting properties for the inhibitor and to develop maximum uniformity of film on the metal surface. This conclusion can be seen by comparing the metal surfaces after the corrosion test. The corrosion product on the sample treated with the Sample #3 inhibitor appeared to be uniform, without pitting, while the corrosion product on Sample #4 had local character.

Polarization curves presented in Figure 2 show that formulations 1, 2 and 4 are effective when they were added to the electrolyte. They lowered the rate of both cathodic and anodic reaction, but had a greater effect on anodic rate. The corrosion potential is more noble with inhibitor than without. This data is in agreement with the statement that imidazolines are classified as film forming inhibitors, and also confirms their ability to donate mainly the negative charge to the metal surface and to lower the rate of anodic reaction.

Polarization curves presented in Figure 3 show that only formulations #1 and #2 have strong film-forming properties and protection. Formulation #4 is not effective under these conditions.

The actual numbers of the corrosion rates and protection power calculated from these polarization curves are presented in Table 4.

The results from the Wheel Corrosion Test (Tables 5, 6) show a high level of protection for samples #1 and #2 even when the concentration level of inhibitors is as low as 15 ppm and very high protective ability in the film persistency test (about 90%).

Table 7 represents the ability of the inhibitors to protect in vapor phase. These results show the effectiveness of the VCI in the formulation.

Table 8 presents data which shows the effectiveness of formulations #1 and #2 under SCC conditions, usually caused by $H_2S$.

It should also be mentioned that the unique molecular structures of TOFAA-based corrosion inhibitors (like Sample #2) allowed this product to perform in high temperature and high pressure environments without coagulating. This product maintains its stability at temperatures up to 400ºF (205ºC) and pressure up to 9,000 psig in sweet ($CO_2$), sour ($H_2S$) and mixed gas systems. This stability will provide corrosion protection performance throughout the range of extreme service conditions encountered in gas well applications.

In addition to the above testing, Ramachandan, et.al. [5, 6] found the mechanism for protection with FAI is based on forming a self-assembled monolayer on the native oxide surface of iron. It protects by forming a hydrophobic barrier preventing migration of $H_2O$, aggressive agents, and electrons to the iron surface. The long chain carboxylic acid also gives a strong bonded film on the surface similar to the FAI [3]. In addition, both the imidazoline and acid covered the steel surface with a strong hydrophobic layer which adsorbed on the metal surfaces and prevented multiple types of corrosion of steel. It should also be mentioned that short chain acids like acetic acid probably only serve as a transport function as it increases the solubility of the imidazoline in the water phase, but does not involve adsorption on the metal.

CONCLUSION

There are two new oil and gas pipeline additives which were formulated utilizing volatile corrosion inhibition technology and imidazoline organic acid chemistry. The formulated inhibitors provided protection in sweet ($CO_2$ presence), sour ($H_2S$ presence) and both a sweet and sour corrosive media, and also prevent stress corrosion cracking due to the hydrogenation of steel.

The study of the formulated inhibitors using different methods confirmed that the mechanisms of protection by FAI/organic acid-based inhibitors are due to their film-forming ability and strongly depends not only on imidazoline (FAI) part, but also on the nature of organic acids.

It is also shown that providing dependable protection in the vapor phase can be achieved by using in the formulation special vapor corrosion inhibitor additives.

## ACKNOWLEDGMENTS

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TABLE 1
EXPERIMENTAL DESIGN DATA

| Dsn Id | Run | Block | Surf. % Factor | Acid % Factor | Amine % Factor | Solv. Factor | Corr. Response | Comp. Response |
|--------|-----|-------|----------------|---------------|----------------|--------------|----------------|----------------|
| 2 | 1 | 1 | 15.00 | 5.00 | 12.00 | 20.00 | 4.00 | 10.00 |
| 5 | 2 | 1 | 5.00 | 5.00 | 35.00 | 20.00 | 6.00 | 10.00 |
| 6 | 3 | 1 | 15.00 | 5.00 | 35.00 | 1.00 | 8.00 | 2.00 |
| 7 | 4 | 1 | 5.00 | 11.00 | 35.00 | 1.00 | 7.00 | 6.00 |
| 1 | 5 | 1 | 5.00 | 5.00 | 12.00 | 1.00 | 5.00 | 0.00 |
| 4 | 6 | 1 | 15.00 | 11.00 | 12.00 | 1.00 | 4.00 | 3.00 |
| 8 | 7 | 1 | 15.00 | 11.00 | 35.00 | 20.00 | 6.00 | 10.00 |
| 3 | 8 | 1 | 5.00 | 11.00 | 12.00 | 20.00 | 4.00 | 10.00 |

Key:    DNS ID - Identification number (assigned to the formulation)
Surf. - surfactant
Solv. - solvent
Amine - FAI
Solvent - Water:Isopropanol (1:1)
Acid - Acetic acid (AA)


TABLE 2
EXPERIMENTAL DESIGN DATA

| Term | Coefficient | Standardize Effect | Sum of Squares |
|------|-------------|--------------------|-----------------|
| A:SURF | 0.0000 | 0.0000 | 0.00000 |
| B:ACID | -0.2500 | -0.5000 | 0.50000 |
| C:AMINE | 1.2500 | 2.5000 | 12.50000 |
| D:SOLV. | -0.5000 | -1.0000 | 2.00000 |
| AB | -0.2500 | -0.5000 | 0.50000 |
| AC | 0.2500 | 0.5000 | 0.50000 |
| AD | 0.0000 | 0.0000 | 0.00000 |


TABLE 3
STUDY OF THE PROTECTION ABILITY OF THE INHIBITORS
IN STATIC AND DYNAMIC CORROSION TEST

| Sample | Protection Power, Z% | |
|--------|----------------------|--|
| | Static Immersion Test ($H_2S$ Presence) | Dynamic Immersion Test ($CO_2$ presence) |
| 1 | 94 | 98 |
| 2 | 97 | 98 |
| 3 | 68 | 62 |
| 4 | 63 | 53 |

$$Z = \frac{\Delta Mc - \Delta Mi}{\Delta Mc} \times 100\%, \text{ where}$$

$\Delta Mc$ = Weight loss of the panel in the electrolyte without inhibitor
$\Delta Mi$ = Weight loss of the panel in the electrolyte with inhibitor

TABLE 4
STUDY OF THE PROTECTION ABILITY OF THE INHIBITORS
WITH ELECTROCHEMICAL TEST METHODS

| Sample | Inhibitor Added to Electrolyte | | Inhibitor Applied to the Electrode | |
|---|---|---|---|---|
| | Corrosion Rate x $10^3$ mmpy | Protection Power, Z% | Corrosion Rate x $10^3$ mmpy | Protection Power, Z% |
| 1 | 85 | 89 | 76.83 | 90 |
| 2 | 128 | 83 | 79.12 | 89 |
| 4 | 115 | 83 | 268.0 | 64 |
| Control | 752.8 | - | 752.8 | - |

TABLE 5
STUDY OF PROTECTION OF INHIBITORS IN THE FILM PERSISTENCY TEST
(WHEEL CORROSION TEST)

| | Concentration of Inhibitors (ppm) | | |
|---|---|---|---|
| Sample | 500 | 2500 | 5000 |
| 1 | 88.5 | 90.2 | 90.2 |
| 2* | 88.1 | 88.1 | 88.1 |
| 3 | 17.1 | 0 | 0 |
| 4 | 0 | 0 | 0 |

*Sample #2 provides 90% and 93% protection even in 100 and 250 ppm, respectively.

TABLE 6
STUDY OF PROTECTION OF INHIBITORS IN CONTINUOUS TREATMENT TEST
(WHEEL CORROSION TEST)

| | Concentration of Inhibitors (ppm) | | |
|---|---|---|---|
| Sample | 15 | 25 | 50 |
| 1 | 90.5 | 91.5 | 91.5 |
| 2 | 90.3 | 93.5 | 94.5 |
| 4 | 88.2 | 91.4 | - |

TABLE 7
PROTECTIVE ABILITY OF INHIBITORS IN THE VAPOR PHASE

| Sample | Time before Corrosion (Hours) |
|---|---|
| #1 + Xylene | >100 |
| #4 + Xylene | <48 |
| Control (Xylene) | 24 |

TABLE 8
STRESS CORROSION CRACKING TEST RESULTS
(CONCENTRATION OF INHIBITORS 200 PPM)

| Sample | Time before Failure (Days) |
|---|---|
| Control | 1 |
| #1 | >20 |
| #2 | >20 |

FIGURE 1 - Typical fatty acid imidazoline

1. Head group
2. Hydrocarbon tail group (fatty acid radical)
3. Pendent group

FIGURE 2 - Polarization curves in the electrolyte
with added inhibitor (200 ppm of inhibitor added to
the solution 5% NaCl + 0.5% $CH_3COOH$)

FIGURE 3 - Polarization curves in the solution
5% NaCl + 0.5% $CH_3COOH$ when the inhibitor is
applied to the electrode