# Corrosion Protection in an Oil System with Water Ingress by Use of Volatile Corrosion Inhibitors

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*Volatile corrosion inhibitors (VCIs) are commonly used in various oil systems to prevent corrosion during preservation and in intermittent operation. However, water ingress still introduces the risk of corrosion when water separates and pools at the bottom of these systems. Traditional corrosion inhibitors used in lubricating oils provide good corrosion protection in the oil phase, but cannot offer protection beneath the oil-water phase line due to their typical hydrophobic nature. It has been determined that the use of proper organic VCIs (which also offer protection in the vapor phase and oil phase) can partition into the water phase and provide additional corrosion protection even in the case of water contamination.*

**Water handling is an important property** for lubricating oils in many applications. Even small amounts of water can cause serious damage in a system, decreasing the oxidative stability of the oil, increasing deposition and contaminants, and reducing the performance of additives.[1] In storage and lay-up, the presence of water can promote surface corrosion on key components inside the system. Over time, each of these factors contributes to shortening equipment life. While operating oils may be replaced, oxidation on metal surfaces may result in costlier and time-consuming repairs.

Studies and laboratory experiments have previously investigated the effectiveness of oil-soluble/water-dispersible corrosion inhibitors to partition into brine and provide protection to pipeline systems.[2] However, key features of these experiments and the application of these inhibitors is their continuous application into flowing/operating systems. Even traditional efficacy tests of these types of inhibitors, such as the continuous wheel test, investigate inhibitor performance under sheer conditions.[3] This opportunity of mixing dispersion is not offered in stagnant preserved systems where water ingress is slow and inconsistent.

Amine-based inhibitors, including imidizolines and aminocarboxylic acids, have been explored for petroleum industries. Inhibitors are carefully crafted to balance a variety of properties for varying systems.[4] Inhibitors for preservation and stagnant applications must be carefully chosen based on the desire for solubility in both oil and aqueous systems.

The use of a specific oil-based corrosion inhibitor additive, with the ability to passively partition from the oil phase into the aqueous phase, is investigated here. The effectiveness of partitioning (at various concentrations of corrosion inhibitor in the preservation oil) is evaluated by analyzing the concentration of the nitrogen-based corrosion inhibitors in the aqueous phase through the Kjeldahl Method for determination of organic nitrogen.[5] The corrosion protection capabilities of the partitioned corrosion inhibitor is quantified and compared at various concentrations using increasingly rigorous iterations of immersion corrosion testing (modeled after ASTM G31[6]) and electrochemical impedance spectroscopy (EIS).

## Experimental Procedure

The evaluation of the corrosion protection provided by a partitioned inhibitor required several different steps. Testing was performed to evaluate the amount of inhibitor that will partition into the aqueous phase under varying circumstances, as well as two separate methods to assess the degree of corrosion protection provided.

### *Extraction of Corrosion Inhibitor from VCI Oil Additive*

#### Determination of Oil/Water Ratio

A common practice for preservation of oil systems includes filling the system with standard lubricating oil treated with a compatible VCI additive. According to the manufacturer's recommendations, VCI oil additives are dosed at 3 to 5% by volume of the base oil inside the system. Other rec-

**TABLE 1** Sample Identification for VCI Oil Additive Extraction

| Sample No. | VCI Oil Additive Concentration (%) | Oil to Water Ratio | Ratio of VCI Additive to Water |
|---|---|---|---|
| 1 | 100 | 1:1 | 1:1 |
| 2 | 100 | 9:1 | 9:1 |
| 3 | 5 | 1:1 | 0.05:1 |
| 4 | 5 | 9:1 | 0.45:1 |

ommendations include directly fogging the VCI oil additive into the preserved system at a specified dosage per volume of the oil system. The amount of VCI additive inside the system will affect the partitioning of the corrosion inhibitor into the aqueous phase. Several ratios of oil phase to water were examined to investigate the partitioning behavior of the corrosion inhibitor. At recommended dosages of 3 to 5%, the partitioning effect of the corrosion inhibitor from the VCI additive will be evaluated with the neat additive and with the additive dosed as recommended by the manufacturer. The ratio of oil phase to aqueous phase was varied as well, investigating 1:1 and 9:1 ratios of oil to water.

### Extraction of Corrosion Inhibitor

A solution of 5% VCI oil additive in standard synthetic poly alpha olefin oil was created. Along with the concentrated oil additive, Table 1 shows the solutions made.

Oil solutions were added to a large beaker and deionized (DI) water was gently poured through the oil layer until the desired oil to water ratio was achieved. Each beaker was covered and allowed to sit for 24 h. After the 24-h period, the oil layer was decanted and separated using a separatory funnel. The remaining aqueous phase was collected, labeled, and submitted for analysis. A sample of the DI water was also submitted for testing to ensure no base level of organic nitrogen is present in the solvent.

Because the volume of water ingress in a preserved system would generally be low compared to the volume of the treated oil, Sample No. 4 is considered the most representative of a real-life preservation system. For preserved systems when the VCI oil additive is fogged and water ingress is experienced, Sample No. 1 could be considered the most representative test sample for the system.

### Determination of Corrosion Inhibitor Concentration

The primary corrosion inhibitor component identified in the VCI oil additive is an organic nitrogen-based corrosion inhibitor compound. Aqueous samples were sent to a third-party analytical laboratory for analysis using the Kjeldahl Method for determining organic nitrogen content in aqueous solutions.

## *Immersion Corrosion Testing*

Two sets of immersion corrosion testing were performed as part of this evaluation. The first evaluation was performed with no duplicates and panel cleaning was performed with 1% hydrochloric acid (HCl), 1% commercial acid corrosion inhibitor, and 98% DI water mixture. The second evaluation was performed in triplicate and panel cleaning was performed with a standard ASTM G01[7] solution.

### Immersion Corrosion Testing—First Iteration

Testing was performed in DI water, with varying amounts of the corrosion inhibitor identified above from the VCI oil additive in solution. The solution was held in a cylindrical glass cell with a 5-in (127-mm) height and 2-in (50.8-mm) diameter. Two hundred g of each solution were used in each test cell to ensure full immersion of the tested panels (0.63 by 1 by 3-in [16 by 25.4 by 76.2-mm] SAE 1008/1010 cold-rolled steel). Panels were prepared by hand polishing both faces to a consistent finish with 240 grit aluminum oxide ($Al_2O_3$) abrasive paper. Panels were cleaned with methanol, weighed to the nearest 0.1 mg, and placed into the respective solutions. Test cells were placed into a 40 ± 2 °C oven for approximately three weeks. At this time, panels were removed, rinsed with methanol, and oxides were removed from the surface via a 1% concentrated HCl solution, also containing 1% corrosion inhibitor to prevent flash corrosion during the cleaning process. The panels were examined for mass loss and the rate of corrosion was calculated using the following formula from ASTM G31 (Equation [2], Section 12.4):

$$Corrosion\ Rate\ (mpy) = \frac{3.45\times10^6\times W}{A\times T\times D} \quad (1)$$

$W$ represents the mass loss in grams, $A$ is the panel surface area in $cm^2$, $T$ is the duration of the test in hours, and $D$ is the metal density in grams per cubic centimeter (7.87 $g/cm^3$ for SAE 1008/1010 steel). The corrosion rate reduction was also calculated by comparing the control sample to the test samples with the following formula:

$$Corrosion\ Rate\ Reduction = \left(1 - \frac{R}{C}\right)\times 100\% \quad (2)$$

where $C$ represents the corrosion rate of the control sample and $R$ is the corrosion rate of the test sample.

A single panel was prepared for each tested solution, along with a single panel to be tested in DI water as a control. A single prepared, but untested, steel panel was subjected to the cleaning procedure as above. The mass loss of the cleaning procedure was determined, and this mass loss was subtracted from the mass loss measured in each tested panel, in order to determine the true mass loss from the immersion corrosion testing.

### Immersion Corrosion Testing—Second Iteration

Testing was performed in DI water, with varying amounts of the corrosion inhibitor identified above from the VCI oil additive in solution. The solution was held in a cylindrical glass cell with a 5-in height and 2-in diameter. Two hundred g of each solution was used in each test cell to ensure full immersion of the tested panels (0.63 by 1 by 3-in SAE 1008/1010 cold-rolled steel). Panels were prepared by hand polishing both faces to a consistent finish with 240 grit

**TABLE 2** Corrosion Inhibitor Content Results

| Sample No. | Ratio of VCI Additive to Water | Inhibitor Detected (ppm) |
|---|---|---|
| 1 | 1:1 | 1,368 |
| 2 | 9:1 | 2,234 |
| 3 | 0.05:1 | 535 |
| 4 | 0.45:1 | 802 |

**TABLE 3** Concentration of Corrosion Inhibitor in Tested Solutions

| Sample Label | Inhibitor Concentration (% by weight) | Inhibitor Concentration (ppm) |
|---|---|---|
| Control | 0 | 0 |
| A | 0.5 | 5,000 |
| B | 0.2 | 2,000 |
| C | 0.1 | 1,000 |
| D | 0.08 | 800 |
| E | 0.05 | 500 |

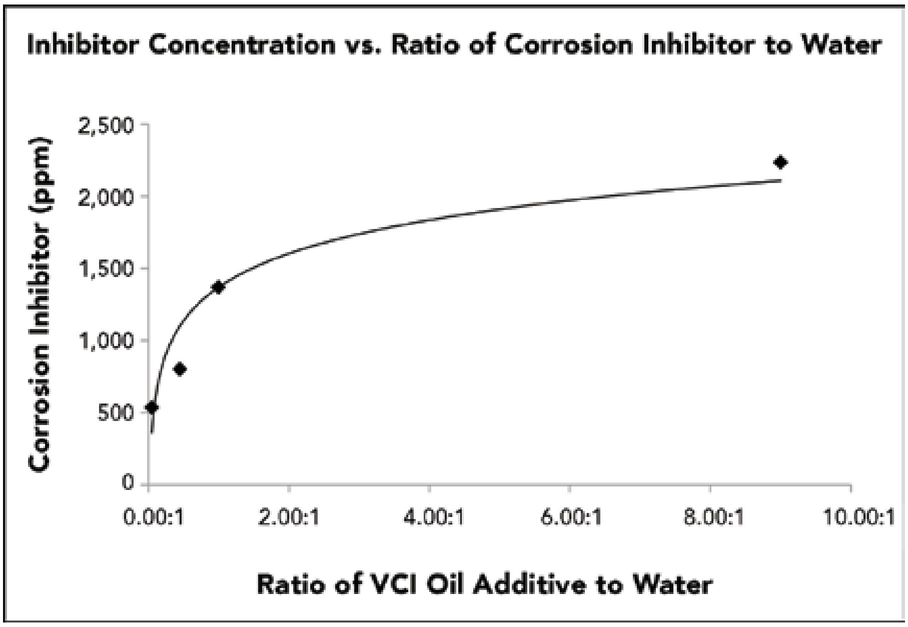

**FIGURE 1** Corrosion inhibitor concentration compared to the ratio of VCI oil additive to water from extraction testing.

$Al_2O_3$ abrasive paper. Panels were cleaned with methanol, weighed to the nearest 0.1 mg, and placed into the respective solutions. Test cells were placed into a 40 ± 2 °C oven for approximately three weeks. At this time, panels were rinsed with methanol, wiped clean with a lint-free wipe, and placed in a cleaning solution as specified in ASTM G01, designation C.3.5 (500 mL HCl, 3.5 g hexamethylene tetramine, and reagent water to make 1,000 mL solution). Panels were then dipped into a solution of commercial corrosion inhibitor at 1% in DI water and dried with a lint-free wipe to prevent further flash corrosion prior to examination of mass loss. The panels were examined for mass loss and the rate of corrosion was calculated as noted in Equation (1).

Three panels were prepared for each tested solution, along with three panels to be tested in DI water as a control. A single prepared, but untested, steel panel was prepared and subjected to the cleaning procedure. The mass loss of the cleaning procedure was determined, and this mass loss was subtracted from the mass loss measured in each tested panel, in order to determine the true mass loss from the immersion corrosion testing.

## Electrochemical Corrosion Testing

EIS was performed on several solutions with different concentrations of the corrosion inhibitor identified above in DI water with 300 ppm sodium chloride (NaCl). EIS testing was performed with 10 mV amplitude around open circuit potential (OCP) over a frequency range of 0.01 to 100,000 Hz on a C1018 steel plug and modeled using the Randles equivalent circuit. The inhibitor efficiency was calculated by comparing the polarization resistance ($R_p$) of the control against the experimental polarization resistance (Equation [3]).

$$\text{Inhibitor Efficiency} = \left(1 - \frac{\text{Control } R_p}{\text{Experimental } R_p}\right) \times 100\% \qquad (3)$$

### *Extraction of Corrosion Inhibitor from VCI Oil Additive*

Extracted solvent samples were submitted for analysis of organic nitrogen content according to the Kjeldahl Method. Results were received in ppm of organic nitrogen in the sample. The amount of corrosion inhibitor (in ppm) was calculated based on the ratio of nitrogen in the corrosion inhibitor molecule (Table 2).

As the ratio of VCI additive to water increased, the concentration of corrosion inhibitor increased in kind. As shown in Figure 1, the inhibitor partitioning seemed to plateau at high VCI additive ratios. Based on the results, a wide range of corrosion inhibitor concentrations were evaluated in immersion testing to observe the effect of varying concentrations on inhibitor on the corrosion protection efficiency.

**TABLE 4** Immersion Testing Results—First Iteration

| Sample | Inhibitor (ppm) | Starting Mass (g) | Ending Mass (g) | Mass Loss (mg) | Corrosion Rate (mpy) | Corrosion Reduction (%) |
|---|---|---|---|---|---|---|
| Control | — | 31.923 | 31.835 | 87 | 1,432.7 | — |
| A | 5,000 | 31.476 | 31.476 | 0 | 0.0 | 100 |
| B | 2,000 | 32.140 | 32.139 | 1 | 16.5 | 99 |
| C | 1,000 | 31.558 | 31.537 | 21 | 345.8 | 76 |
| D | 800 | 32.461 | 32.410 | 51 | 839.9 | 41 |
| E | 500 | 32.159 | 32.140 | 20 | 329.4 | 77 |

**TABLE 5** Immersion Testing Results—Second Iteration

| Sample | Sample No. | Inhibitor (ppm) | Starting Mass (g) | Ending Mass (g) | Mass Loss(A) (mg) | Corrosion Rate (mpy) |
|---|---|---|---|---|---|---|
| Control | 1 | — | 32.298 | 32.207 | 89 | 1,613.9 |
| | 2 | | 32.394 | 32.313 | 78 | 1,414.4 |
| | 3 | | 32.316 | 32.246 | 68 | 1,233.1 |
| A | 1 | 5,000 | 32.235 | 32.233 | 0 | — |
| | 2 | | 32.090 | 32.087 | 0 | — |
| | 3 | | 32.378 | 32.376 | 0 | — |
| B | 1 | 2,000 | 32.272 | 32.270 | 0 | — |
| | 2 | | 32.173 | 32.171 | 0 | — |
| | 3 | | 32.108 | 32.105 | 0 | — |
| C | 1 | 1,000 | 32.014 | 32.012 | 0 | — |
| | 2 | | 31.889 | 31.887 | 0 | — |
| | 3 | | 31.969 | 31.967 | 0 | — |
| D | 1 | 800 | 32.125 | 32.123 | 0 | — |
| | 2 | | 32.319 | 32.317 | 0 | — |
| | 3 | | 32.144 | 32.142 | 0 | — |
| E | 1 | 500 | 32.094 | 32.084 | 7 | 126.9 |
| | 2 | | 32.153 | 32.150 | 0 | — |
| | 3 | | 32.280 | 32.278 | 0 | — |

(A) Calculation includes the correction for mass lost during the panel cleaning procedure.

It is noted in Table 2 that Sample No. 1 and Sample No. 4 are the most representative for recommended applications. The control sample analyzed was found to have no organic nitrogen content, as expected.

### *Immersion Corrosion Testing*

Based on the results of the extraction testing, the following concentrations were selected to evaluate the effectiveness of the partitioned corrosion inhibitor in solution. Samples were prepared as described in Table 2 and labeled as shown in Table 3.

#### FIRST ITERATION OF TEST

Immersion testing was conducted for 479 h to assess the level of corrosion protection provided at various concentrations. As shown in Table 4, increasing inhibitor concentration in general showed improved corrosion protection. Corrosion rate reduction was above 75% for most samples. While it would be expected to see the corrosion rate in Sample E be higher than that of Sample D, this was not the case in the first iteration of immersion corrosion testing.

Note that the mass loss from the panel cleaning procedure was determined to be negligible. Mass loss values represent the mass loss values measured during testing.

To better explore the results, the second iteration of immersion corrosion testing was performed.

#### SECOND ITERATION OF TEST

The second iteration of immersion corrosion testing was conducted for 435 h. As shown in Table 5, more careful sample preparation and cleaning, as well as eval-

**TABLE 6** EIS Testing Results

| Inhibitor (ppm) | OCP (mV) | $R_P$ (kΩ) | Inhibitor Efficiency (%) |
|---|---|---|---|
| 0 | –451.0 | 0.794 | 0.0 |
| 100 | –428.0 | 1.396 | 43.1 |
| 500 | –379.4 | 12.25 | 93.5 |
| 2,000 | –376.7 | 25.64 | 96.9 |
| 5,000 | –231.8 | 43.24 | 98.2 |

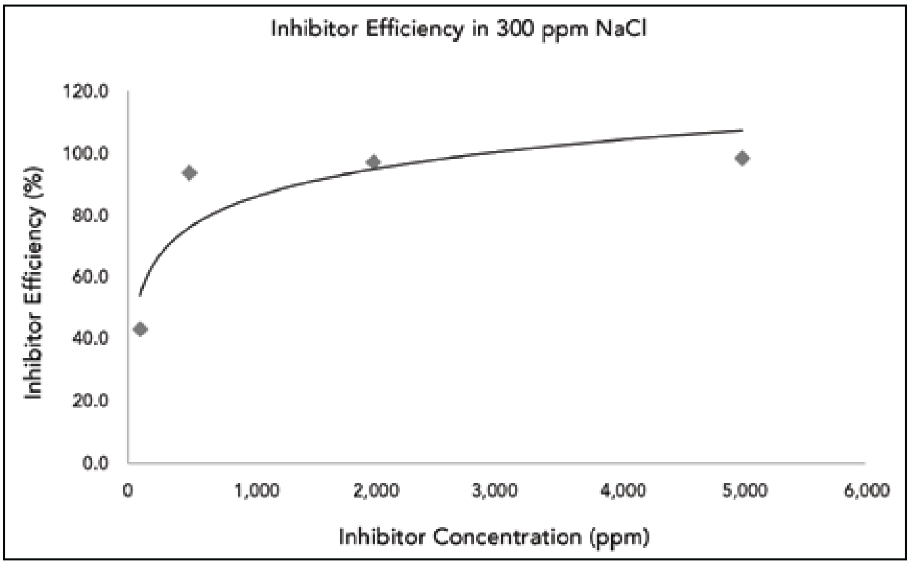

**FIGURE 2** Inhibitor efficiency compared to the concentration of corrosion inhibitor from EIS testing.

uation of samples in triplicate provided much more consistent results. The presence of corrosion inhibitor at the lowest concentrations of 500 ppm showed a significant effect on the corrosion rate, eliminating corrosion on all but one sample.

The mass loss of the cleaning procedure was determined to be ~3 mg. The mass loss is the measured mass loss after testing, minus this 3-mg value. Due to rounding, some mass loss values after this correction would be listed as "–1 mg," typically indicating a mass gain. These values are reported as 0 mg in Table 5.

Inhibitor concentrations of 800 ppm or greater provided excellent corrosion protection, resulting in a corrosion rate of 0 mpy, corresponding to a corrosion rate reduction of 100%. One sample with inhibitor concentration of 500 ppm did show some corrosion over the course of testing, corresponding to a corrosion rate of 126.9 mpy, or a corrosion rate reduction of 91.1% (calculated with Equation [2] using the average corrosion rate of control Samples No. 1, 2, and 3).

## Electrochemical Corrosion Testing

EIS testing was performed on the corrosion inhibitor of interest at various concentrations. The test solution utilized a 300-ppm concentration of NaCl in DI water to increase the conductivity and corrosivity of the system. The results of this testing show a marked increase in the polarization resistance to 1.396 kΩ with just the addition of 100 ppm inhibitor and an even higher resistance when the inhibitor is dosed according to the concentrations tested above. This data is represented in Table 6 and Figure 2.

## Conclusions

Extraction testing, based on the manufacturer's various recommended applications of the VCI oil additive, shows that corrosion inhibitor partitioning results in a concentration of roughly 800 to 1,350 ppm in the aqueous phase, depending on the application method of the VCI oil additive. These results provide a benchmark for corrosion testing, to test the partitioned corrosion inhibitor for its protection capabilities in a controlled setting.

Initial immersion corrosion testing provided promising results, showing >75% corrosion rate reduction at even the lowest concentration of inhibitor. When reevaluation was performed in triplicate, even better results were seen, showing a complete reduction in corrosion rate in all but one case.

It is likely that initial factors such as cleanliness of metal surfaces or the presence of other materials or contaminates can influence the corrosion rate. In the context of the real-world application being evaluated, metal surfaces may not be completely clean, and contaminates may be carried into the system by the water as it ingresses. While all these factors may affect the corrosion protection provided by the corrosion inhibitor that partitions from the oil phase to the intruding aqueous phase, it is shown that corrosion inhibitor that naturally partitions into the aqueous phase from the treated oil phase may provide corrosion protection in that system.

Results from EIS reinforced the results obtained via immersion testing. Concentrations of inhibitor that were much lower than what would be expected in a layup scenario returned polarization resistance values that were notably higher than the non-treated solution. It should also be noted that the chloride concentration utilized in the EIS testing performed would only be seen in very contaminated systems in actual application. The significant levels of corrosion inhibition observed in such a contaminated system effectively demonstrate the potential protection that can be realized by the passive partitioning of inhibitor from the oil phase into the aqueous phase.

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