

Film persistency of new high-temperature water-based batch corrosion inhibitors for oil and gas wells

Sunder Ramachandran · Carlos Menendez ·
Vladimir Jovancicevic · Jeff Long

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Abstract Water-based corrosion inhibitors, in addition to providing improved performance, offer several other advantages over oil-based corrosion inhibitors, such as better water-partitioning characteristics, high flash points, and higher reportable quantities if a spill occurs. We have found in several instances that new water-based corrosion inhibitor products provide longer treatment lives and better protection than similar inhibitors in oil-based formulations. Corrosion inhibition in high-temperature (HT) oil and gas wells has been frequently accomplished using oil-based corrosion inhibitors. This paper presents some earlier laboratory work and field performance data on new water-based corrosion inhibitors relative to conventional oil-based HT corrosion inhibitors. A laboratory investigation using white light interferometry is also presented on the film thickness and uniformity measurements of corrosion inhibitor films. This information is compared with field performance of the corrosion inhibitor.

Keywords High temperature · Corrosion inhibition · Batch treatment · Film persistency · CO₂ corrosion

Introduction

Nickel-based alloys often become difficult to use in ultra high-pressure and high-temperature (HT) wells. It can take

over a year to obtain nickel-based alloy tubing and casing strings from the manufacturer (Zeringue 2006). Nickel-based alloys are also susceptible to stress-crack corrosion in the presence of hydrogen sulfide.

Carbon steel, in conjunction with corrosion inhibitors, has been used in several wells above 300 °F (150 °C) (Goodfellow and Barr 2001; Place 1992; Smith 1982; Ramachandran et al. 2006). Oil-soluble corrosion inhibitors have been developed and used in HT gas wells. In previous work (Ramachandran et al. 2006), we have documented the performance of oil-soluble corrosion inhibitors in extremely challenging laboratory corrosion tests. The performance of HT oil-soluble corrosion inhibitors in field situations with high bottom hole temperatures, high partial pressures of carbon dioxide, and some hydrogen sulfide and brines of different salinities has also been documented in this work (Ramachandran et al. 2006). Corrosion inhibitors that work in these systems often have large alkyl tail groups that help bind the monolayer or bi-layer film on the surface (Ramachandran et al. 1996; Jovancicevic et al. 1998; Ramachandran and Jovancicevic 1998).

Methods have been developed to formulate organic molecules with large alkyl tails in water-based products (Yang and Jovancicevic 2009). We have found in several instances that new water-based corrosion inhibitor products provide longer treatment lives and better protection than similar inhibitors in oil-based formulations (Yang et al. 2007). A new water-dispersible, HT corrosion inhibitor was developed that had similar HT stability and corrosion inhibitor properties as a successful oil-soluble corrosion inhibitor (Ramachandran et al. 2009).

Optical profiling (White Light Profilometry) is a technique used to determine the three-dimensional profile of objects in a non-invasive manner. The method has been

S. Ramachandran (✉) · C. Menendez · V. Jovancicevic
Baker Hughes, 12645 West Airport Blvd.,
Sugar Land, TX 77478, USA
e-mail: Sunder.Ramachandran@bakerhughes.com

J. Long
Baker Hughes, 2101 Market Street, Building B,
Midland, TX 79703-7510, USA

extended to measure the thickness of semi-transparent batch inhibitor films (Menendez et al. 2010).

This paper provides information that compares the laboratory and field performance of water-based corrosion inhibition treatment with oil-based corrosion inhibitor performance. The new corrosion inhibitor highlighted can provide corrosion protection at temperatures as high as 400 °F (204 °C). The paper also uses optical profiling to compare the film thickness and uniformity of oil-based and water-based corrosion inhibitors obtained under simulated field conditions.

Experimental

The film persistency of corrosion inhibitors was tested using the wheel bomb (WB) apparatus (Ramachandran et al. 2009). C1018 carbon steel coupons were initially weighed. The coupons were then filmed with corrosion inhibitor at different concentration of inhibitors in soda bottles under saturated CO₂ and 180 °F (82 °C) conditions for 1 h. In this test, filming occurs from dispersed solution of concentrated corrosion inhibitor in a brine solution. The coupons were then rinsed with de-ionized water and transferred to the WB in inhibitor-free brine/oil mixture. The tests were performed at 350 °F (177 °C). The tests were performed with CO₂ at a pressure of 100 psi (687 kPa). The composition of brine used in the test is shown in Table 1.

The brine/oil ratio was 90/10 in these tests. The hydrocarbon used in the tests was an aliphatic hydrocarbon solvent (Isopar M). The test was run for 18 h. At the end of the test, the coupons were wiped clean, briefly immersed in inhibited acid solution and then weighed. The corrosion rate was measured using weight loss.

The WB test is also used to test the ability of coupons filmed in neat corrosion inhibitor solutions to prevent corrosion. In these tests, the coupon was filmed in neat inhibitor for 1 h under a CO₂ atmosphere at appropriate conditions. The coupons were rinsed with DI water and tested. In one WB test, the brine shown in Table 1 is used. The test was performed at room temperature 77 °F (25 °C) and with 15 psi CO₂ (104 kPa). Another WB test was performed under the condition of the pressurized WB test in a published work (Yang et al. 2007).

Table 1 Composition of brine used in film persistency WB test

Component	Concentration (mg/l)
CaCl ₂ ·2H ₂ O	2,190
MgCl ₂ ·6H ₂ O	580
NaHCO ₃	330
NaCl	15,390

The analysis of the film thickness was achieved using techniques similar to those published previously (Menendez et al. 2010). A WYKOTM NT9100 optical profiler (WLI) was equipped with various objectives, and an automated stage was employed in this study. Interference in WLI is used to determine when a point on the sample is in exact focus, as the instrument is adjusted to give maximum constructive interference at best focus. By scanning the lens towards the surface, the height of all pixels in the image can be determined with high precision, provided that enough light is reflected back into the lens from that point. This technique has a depth resolution of 3 nm. The authors (Menendez et al. 2010) describe the software needed to analyze a thick film. This option is used in this work. The thick film code is used to measure the thickness of the transparent film at each point of the film laid over the sample. The detection limit of this method is ~2 μm. In Fig. 1, a schematic diagram of the film thickness measurement technique is shown.

Film thickness measurement requires calibration because light travels through a film that features a refraction index different from air. To conduct the calibration, a portion of the surface is imaged, which leaves an area without film to create a step to the bare substrate (see Fig. 2). A thick film measurement is performed where single envelope data are set to surface 2 (inhibitor/metal interface). 2D cursors are used later to examine the film-to-no-film interface. The value of the refraction index of inhibitor film is adjusted until the substrate appears continuous across the film boundary.

The images shown in Fig. 3 serve as examples of the two sets of fringes that are detected as the instrument runs through focus on top of the film and on the film–metal interface. The thick film analysis tool provides images for the top of the film and the surface of the steel substrate.

An image (i.e., film thickness) obtained by subtracting the two images is also provided. The image provided for the top of the film (film surface views) was used to describe such film features as uniformity and continuity. In areas

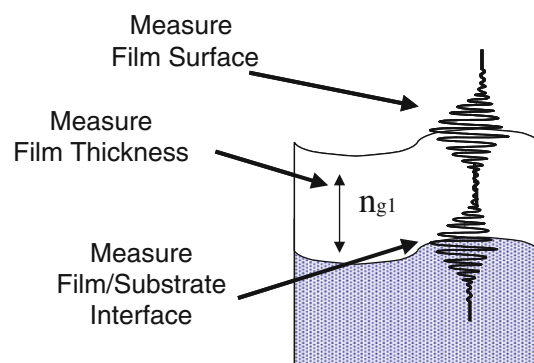


Fig. 1 Schematic of a film thickness measurement

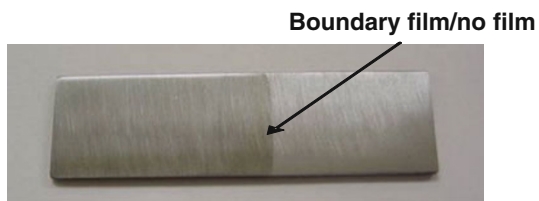


Fig. 2 Inhibitor film creates step on bare substrate

where the film has either become thinner than $2\ \mu\text{m}$ or has been removed from the surface, the software shows the steel surface data captured for that location, thus providing a realistic view of the film. Another feature of the tool allows for the creation of a histogram (height distribution) from the thickness values representing every pixel of the image (data set). The histograms are useful in analyzing film uniformity.

Results

The corrosion inhibitor results presented in this paper are for a standard oil-soluble corrosion inhibitor consisting of a conventional imidazoline-based corrosion inhibitor [CIA (CRW9229)] and a new water-soluble fatty acid/amidamine corrosion inhibitor [CIB (CGO9051U)]. The actives in the two corrosion inhibitors are the same, but surfactant/solvent packages are different. The results of WB corrosion tests, i.e. film persistency test obtained at $350\ ^\circ\text{F}$ ($177\ ^\circ\text{C}$) and $100\ \text{psi}$ ($687\ \text{kPa}$) CO_2 are shown in Table 2. Coupons in these tests were filmed at concentrations of 2,500 and 5,000 ppm before being introduced into the WBs.

In this test, the water-soluble corrosion inhibitor (CIB) has better performance than the oil-soluble corrosion inhibitor (CIA) at same concentrations.

Optical profiling was used to determine the potential film thickness differences between CIB and CIA. This method was used to compare film thicknesses obtained with CIA and CIB after filming the coupons for a period of 10 s and drying for 10 min in neat corrosion inhibitors. The results obtained are shown in Fig. 4.

Fig. 3 Fringes from a film thickness measurement. **a** Top of the film fringes; **b** film–metal interface fringes

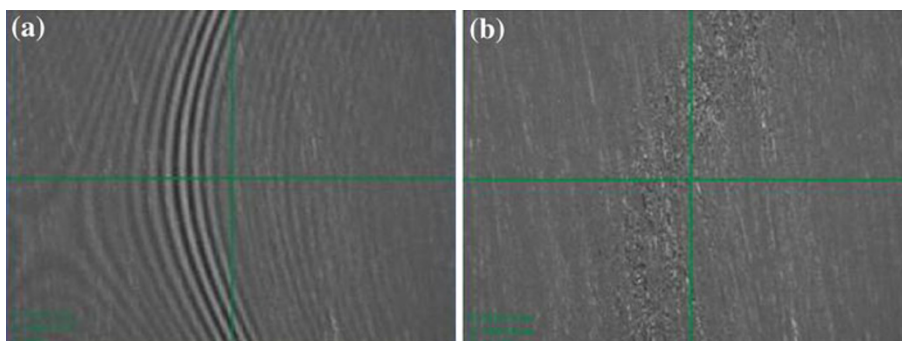


Table 2 Film persistency WB test of CIA and CIB

Inhibitor	Concentration (ppm)	Corrosion rate (mpy)	% Protection
Blank	0	109.2	0
CIA	2,500	4.3	96.1
CIA	5,000	3.9	96.4
CIB	2,500	1.9	98.2
CIB	5,000	1.1	98.9

Brine/oil ratio = 90/10, $100\ \text{psi}$ ($687\ \text{kPa}$) CO_2 , $350\ ^\circ\text{F}$ ($177\ ^\circ\text{C}$), 16-h test

The results indicate a thicker film of $3.9\ \mu\text{m}$ with the oil-soluble corrosion inhibitor CIA and $1.9\ \mu\text{m}$ with the water-dispersible corrosion inhibitor CIB.

After filming, the coupons were placed in a 24-h WB test at $25\ ^\circ\text{C}$ with $1,662\ \text{kPa}$ CO_2 . The surfaces that corroded were evaluated using the copper displacement method. The images of the coupons after using the copper displacement test are shown in Fig. 5.

The images in Fig. 5 show that treatments with CIB better protect the coupon than CIA in the WB test using coupons filmed from neat corrosion inhibitor solutions. CIB is dramatically superior to CIA. This contrasts with the tests where the coupon is filmed from a brine containing concentrated corrosion inhibitor. The film thickness after the WB test is then measured. For the coupon treated with CIA, there was no corrosion inhibitor left, so one was unable to make a measurement of its thickness. The film thickness of the coupons treated with CIB as determined using the optical profiler is shown in Fig. 6.

It will be noticed that the corrosion inhibitor film of the coupon filmed with CIB has increased from 1.9 to $3.2\ \mu\text{m}$, while the thickness of the coupon filmed with CIA is not seen after the test. Clearly, for the given conditions where both coupons are filmed in neat corrosion inhibitor (i.e. batch application), the water-based corrosion inhibitor CIB provided better protection than the oil-based corrosion inhibitor CIA. This is an interesting observation as before the test one would have thought that the coupon with the thicker corrosion inhibitor film would provide better protection.

Fig. 4 Optical profiler results of film thickness using neat CIA and CIB

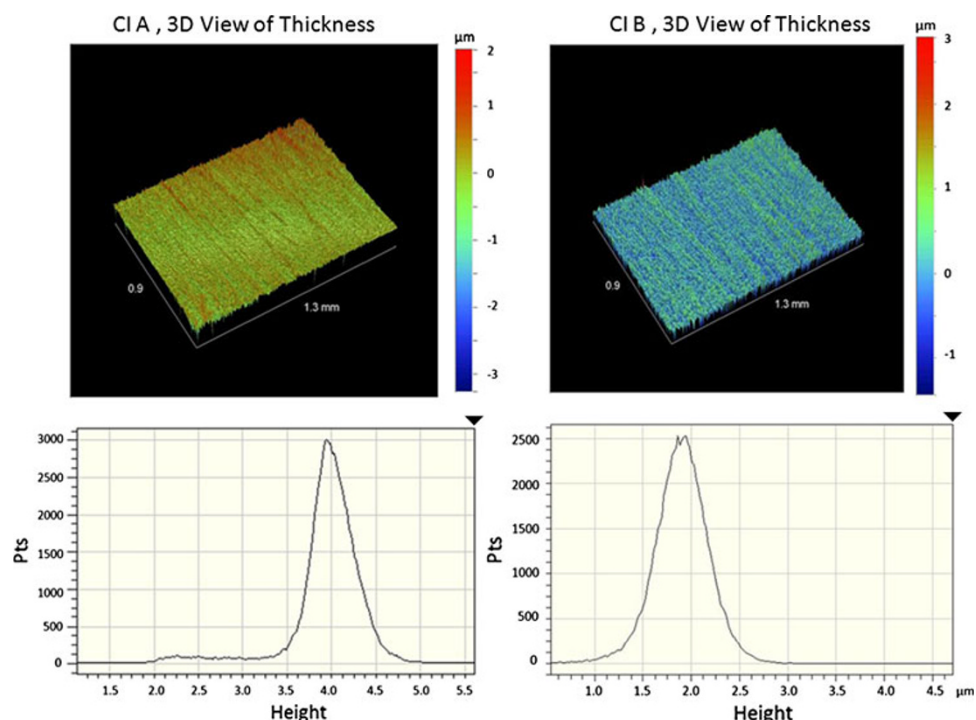


Fig. 5 Images of coupons treated with corrosion inhibitors CIA and CIB after the 24-h wheel test and the copper displacement test



In previous work (Yang et al. 2007), it was found in field tests that a batch treatment of three gallons of water-dispersible corrosion inhibitor [CID (CRW9196)] was as effective as five gallons of a similar oil-soluble corrosion inhibitor [CIC (CRO193)]. This was a surprising result that was attributed to the fact that the oil-soluble corrosion inhibitor produced large spherical emulsion droplets of approximately 100 μm in diameter, while the water-dispersible corrosion inhibitor had much smaller droplets (1–2 μm). Due to the difference in size, the water-dispersible corrosion inhibitor can have 10^5 – 10^6 more droplets dispersed in the brine. This likely improves the batch treatment performance.

The differences in oil-soluble corrosion inhibitor (CIC) and water-soluble corrosion inhibitor (CID) were studied using the optical profile method. Coupons were filmed in

neat corrosion after filming for 10 s and drying for 10 min. The coupons were then placed in a WB test at 220 °F (104 °C) and 15 psi CO₂ (104 kPa). The results of the copper displacement are shown in Fig. 7.

Both coupons were protected; the optical profiler was used to measure the film thickness of the coupons after the test. These results are shown in Fig. 8.

The results provided in Fig. 8 appear to show that a more uniform and thicker film is obtained using the water-dispersible corrosion inhibitor CID (6.7 μm) than the less uniform film obtained with the oil-soluble corrosion inhibitor CIC that has a film thickness varying between 3.9 μm to 5.7 μm . The results obtained from the 24-hour wheel test and the optical profiler measurements of the representative film thickness are summarized in Table 3.

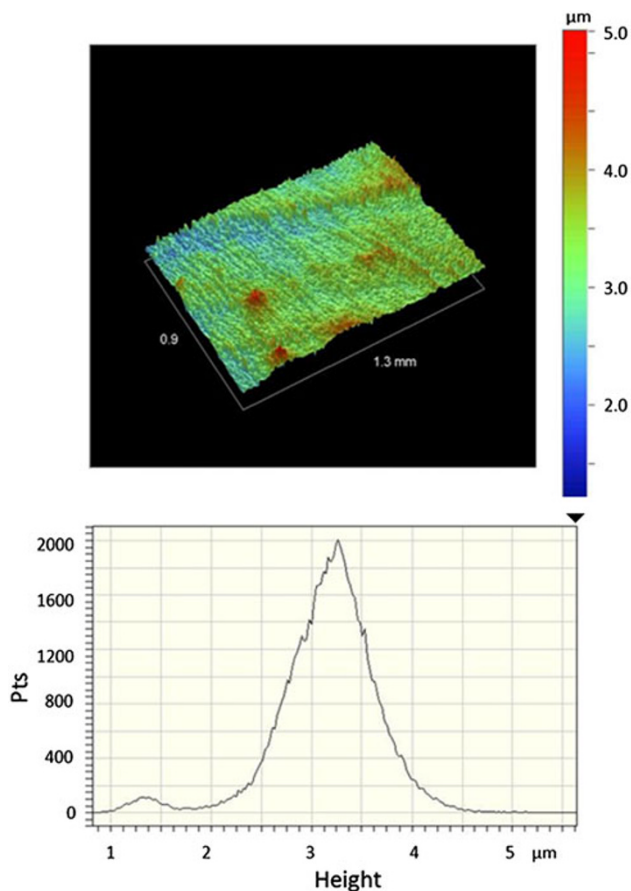


Fig. 6 Film thickness of coupons treated with CIB after 24-h wheel test

It can be seen from the results that the water-soluble corrosion inhibitor (CID) has a thicker and more uniform film after the test than the oil-soluble corrosion inhibitor (CIC). This likely results in the increased film persistence of the product as is seen in field tests (Yang et al. 2007).

Discussion

In previous work, it was found that a new water-dispersible corrosion inhibitor had better film persistency than the

equivalent oil-based corrosion inhibitor (Yang et al. 2007). Oil-soluble corrosion inhibitors have been developed and used in HT gas wells. In previous work, we have documented the performance of oil-soluble corrosion inhibitor CIA in extremely challenging laboratory corrosion tests where the partial pressure of carbon dioxide was 10.3 MPa (1,500 psi CO₂) and the partial pressure of hydrogen sulfide (H₂S) was 0.0021 MPa (3 psi H₂S) with rotation rates of 2,000 rpm in an 80/20 mixture of brine and condensate (Ramachandran et al. 2006). Oil-soluble corrosion inhibitor CIA has been used in a variety of HT systems. In our earlier work, we documented its successful performance in different wells in systems with high bottom hole temperatures, high partial pressures of carbon dioxide, and some hydrogen sulfide and brines of different salinities (Ramachandran et al. 2006). CIA has been used frequently in batch treatments of deep HT wells.

A new water-dispersible, HT corrosion inhibitor CIB was developed that had similar HT stability and corrosion inhibitor properties as CIA (Ramachandran et al. 2009). Optical profiling is a technique used to determine the three-dimensional profile of objects in a non-invasive manner. This method has been extended to measure the thickness of semi-transparent batch inhibitor films (Menendez et al. 2010).

The resolution of the technique is in the micron range, so it does not cover the nanometer-thick monolayer or bi-layer corrosion inhibitor films that may exist. The results here show a thinner film with the water-based corrosion inhibitor (CIB) than the oil-based corrosion inhibitor (CIA) after filming in neat solution. After placing the filmed coupons in a WB, we see better protection with the water-based corrosion inhibitor (CIB) than the oil-based corrosion inhibitor (CIA). The film thickness of the coupon filmed with CIB also grows thicker from 1.9 to 3.2 μm after being placed in the WB corrosion test. This may indicate that the film incorporates oil in the inhibitor film.

In the work characterizing corrosion inhibitors CIC and CID of earlier work (Yang et al. 2007), the new water-based corrosion inhibitor (CID) has a thicker and more uniform film than the oil-based corrosion inhibitor (CID) after the 24-h wheel test. This may explain the greater film

Fig. 7 Images after copper displacement

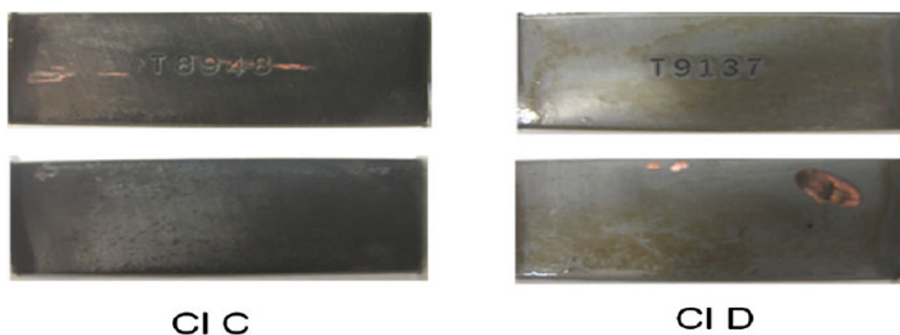


Fig. 8 Optical profiler results of film thickness using CIC and CID

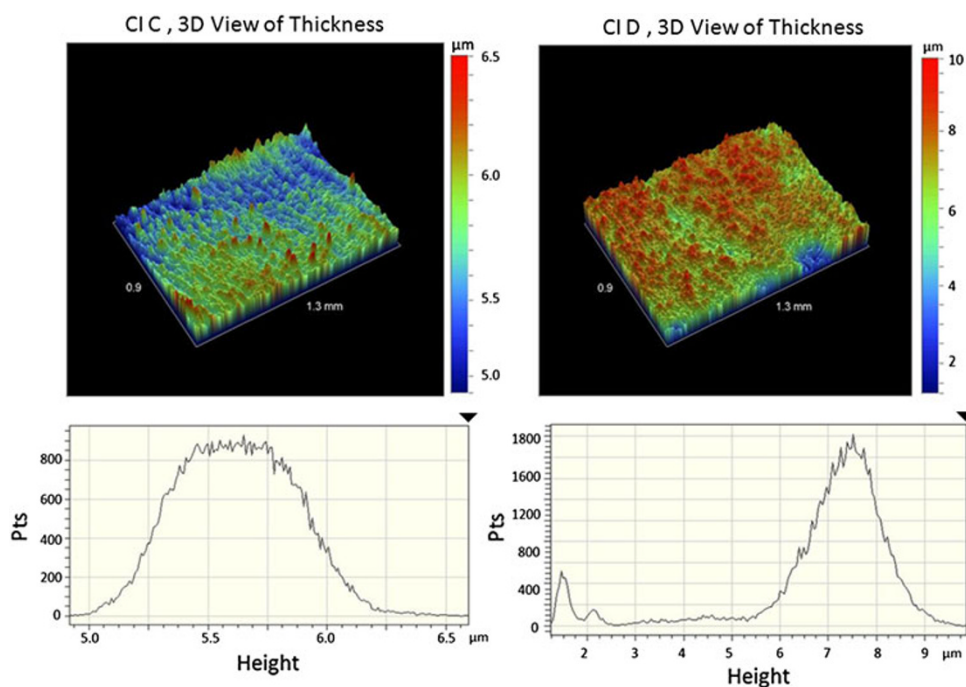


Table 3 Results of WB test and WLI film thickness for CIC and CID

Inhibitor	Corrosion rate (mpy)	% Protection	Film thickness (μm)
Blank	42.6	0	
CIC	3.9	90.8	2.7 ± 0.6
CID	4.0	90.6	3.3 ± 0.4

persistence of the water-based corrosion inhibitor (CID) than the oil-based corrosion inhibitor (CIC) seen in the field (Yang et al. 2007).

Conclusion

An oil-soluble corrosion inhibitor CIA has been used in a variety of HT systems (Ramachandran et al. 2006). A new water-dispersible, HT corrosion inhibitor CIB was developed that had similar HT stability and corrosion inhibitor properties as CIA. Optical profiling was used to compare the film thickness and uniformity of oil-based and water-based corrosion inhibitors that work in applications as high as 204 °C. The water-soluble corrosion inhibitor (CIB) had a thinner film (1.9 μm) than the oil-soluble corrosion inhibitor (CIA) (3.9 μm) immediately after the filming test in neat corrosion inhibitor. After a 24-h WB test, however, it was seen that this thinner film was better able to protect the coupon after exposure to a WB test and the film grew to a thickness of 3.2 μm .

The optical profiler was also used to compare the oil-soluble corrosion inhibitor (CIC) and water-based corrosion

inhibitor (CID) studied earlier by Yang et al. (2007). It was found in this work that the water-dispersible corrosion inhibitor (CID) had better film persistency than the equivalent oil-based corrosion inhibitor (CIC) in field tests. It was also found that the water-dispersible corrosion inhibitor (CID) has several orders of magnitude more droplets in brine. In our work, we have found that the water-dispersible corrosion inhibitor (CID) has a thicker and more uniform film (6.7 μm) than the oil-based corrosion inhibitor (CIC) where the corrosion inhibitor film varies between 3.9 and 5.7 μm after a 24-h WB tests.

The results show that systems with a thicker, more-uniform intact corrosion inhibitor films after a performance test such as the WB test will be more film persistent than those systems that have thinner corrosion inhibitor films after the test.

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