HIGH PERFORMANCE BATCH TREATING CORROSION INHIBITOR

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ABSTRACT

A new high performance corrosion inhibitor was developed for oil and gas field batch treatment applications. The performance of the new corrosion inhibitor was enhanced by its superior dispersion properties. Laboratory corrosion inhibition and film coverage tests showed that new corrosion inhibitor provides better corrosion inhibition than conventional corrosion inhibitor. The new corrosion inhibitor exhibited improved partitioning into water phase due to its more stable dispersion in aqueous phase. The higher dispersibility is an indication of improved field performance. It was verified in the field test that this new inhibitor provided significantly better performance than conventional batch corrosion inhibitors.

Keywords: High performance, batch treatment, corrosion inhibitor

INTRODUCTION

Corrosion is a serious problem for oil and gas productions in the presence of CO_2 and H_2S gas. Corrosion inhibitors are commonly used to slow down the corrosion process of mild steel in oilfield environment.[1] The corrosion inhibitors reduce corrosion of metal by forming a protective film that can isolate the metal from the aqueous corrosive environment.

Traditional oil soluble corrosion inhibitors are commonly used for batch treatment of oil and gas wells. Oil soluble corrosion inhibitors have improved film forming and film persistency properties than water soluble corrosion inhibitors. However, most mature oil and gas wells produce more water than oil or condensate. These high water cut wells need large amounts of oil soluble corrosion inhibitor to provide adequate corrosion protection in the comparatively large aqueous phase.[2] The oil soluble corrosion inhibitors usually contain highly volatile hydrocarbon solvent that can cause potential environment hazard (e.g. low reportable quantities in case of spill).

In this work, a highly water dispersible corrosion inhibitor was developed, which gives better film persistency properties than their oil soluble corrosion inhibitor counterparts. The new corrosion inhibitor is dispersed and transported more effectively in typical oilfield applications (e.g. high fluid level wells) with superior performance.

EXPERIMENTAL

Chemicals and Materials

Two corrosion inhibitors were compared in this study in terms of their overall performance. One is a conventional oil soluble corrosion inhibitor (A), amidoimidazoline derivative, dissolved in an aromatic solvent. The other is the water dispersible corrosion inhibitor (B), consisting of the same active, dissolved in water using proprietary technology.[3] The material of metal coupons used in this study is C1018 carbon steel.

The hydrocarbon used in this work is Isopar M, a mixture of hydrocarbons supplied by EXXON Chemical Co. NACE brine was used in this work, which consists of 4.07 g/l $CaCl_2.2H_2O$, 1.86 g/l $MgCl_2.6H_2O$, and 94 g/l NaCl.

Corrosion Inhibition Tests

Rotating Wheel Test. Rotating wheel testing was performed to evaluate the film persistency of the test inhibitors . The test solution was150 ml CO_2 saturated solution of 10/90 Isopar M/NACE brine. The brine and oil were sparged with CO_2 for 1 hour prior to use. The coupons (Area = 3.0 in^2) were pre-cleaned with chloroform in ultrasonic bath. The coupons were placed in brine/oil mixture in a glass bottle. The corrosion inhibitors were added at 5,000ppm (vol) under CO_2 sparged. The bottles were sealed and rotated for 16 hours at 60 °C. The test fluid was replaced by pre-purged fresh fluid twice during the first two hours. After the test, the coupon was cleaned sequentially with inhibited 15% HCl solution, $NaHCO_3$ saturated solution, deionized water and IPA. Each test was run in duplicate, and the corrosion rates were averaged. The corrosion rate and percentage of protection was calculated from weight loss by following equations:

$$\text{Corrosion rate (CR), MPY} = \Delta W*534/(\rho*A*T) \qquad (1)$$

$$\text{Percent protection, \%P} = (CR_{blank}-CR_{inhib})*100/CR_{blank} \qquad (2)$$

Where ΔW is weight loss before and after corrosion in mg, ρ is density of metal coupon in g/cm^3 (7.86 g/cm^3 for mild steel), A is coupon area in square inches, T is time of exposure in hours and MPY is mils per year.

Film Coverage Test. Film coverage of the corrosion inhibitor was evaluated qualitatively with the copper ion displacement test using 10% $CuSO_4$ solution after the above corrosion test. Film coverage was estimated from the area of the coupon exhibited no copper displacement (clean metallic surface).

Pressurized Wheel Bomb Test. Corrosion inhibition performance was evaluated in pressurized wheel bomb testing. The weight loss method was used to measure corrosion rate. 55 ml of CO_2 sparged 10/90 Isopar M/water mixture was filled into the bomb, and charged with 14.7 psi (101.3 kPa) CO_2 at ambient temperature. The test pressure vessel was then installed on the wheel rig and rotated. The test temperature was 104 °C and test duration was 24 hours. The surface area of the test coupon was 2.42 in^2.

Sparged Beaker Test. Film persistency was also evaluated in sparged beaker testing. 900 ml of brine and 100 ml of Isopar M were added to each cell and sparged with CO_2 and heated to 60°C. The corrosion rate was monitored by linear polarization resistance (LPR) method with a Gamry electrochemical testing system. After about 30 minutes of pre-corrosion, the inhibitor was added to cells at a concentration of 5,000 ppm. LPR monitoring continued for 20 hours. To study the film persistence of the inhibitors, the fluid was replaced with fresh test solution every 20 hours and corrosion rate was continuously monitored.

Inhibitor Partitioning. The partitioning of inhibitor into the water phase was determined by adding of different amounts of inhibitors into CO_2 saturated solutions of 10/90 Isopar M/NACE brine, and shaking for 20 times and then separating the aqueous phase after 1 hour. Coupons were introduced into the aqueous solution, and exposed at 60 °C for 4 hours. The coupon film coverage was examined bu using the copper ion displacement method.

Dispersibity Test. The dispersibility of inhibitors was observed visually by the addition of inhibitors into CO_2 saturated solutions of 10/90 Isopar M/NACE brine (v/v) with gentle mixing. The particle size of the dispersion was measured with an optical microscope.

Emulsion Test. Emulsion tendency was performed with the bottle test method. The new inhibitor was added at a concentration of 5,000 ppm to 10/90 Isopar M/NACE brine mixture, and shaken for 20 times. The emulsion tendency was determined by the observation of separation at the oil/water interface with time.

RESULTS AND DISCUSSION

In order to study the suitability of corrosion inhibitors for batch treatment, pressurized wheel bomb, rotating wheel, sparged beaker and copper displacement tests were conducted to study film coverage and persistency in laboratory. In the research and development of new inhibitors, Isopar M was used because it contains both linear and cyclic hydrocarbons to simulate generic crude oil.

Corrosion and Film Persistency Tests

The film persistency test was performed by using the wheel test at 60 °C in a CO_2 saturated oil/brine mixture. The weight loss results were shown in Table 1. In this test corrosion protection was 99% for the new water dispersible corrosion inhibitor, and 44% for the conventional oil soluble inhibitor. The copper ion displacement tests were used to semi-quantitatively estimate the corrosion inhibitor film coverage. In the test, the uncovered metal iron surface was shown by brown colored copper deposit. The photographs of the coupons subjected to film persistency test and after being exposed to copper ion displacement solution are shown in Figure 1. There is no evidence of corrosion on the coupon exposed to the new inhibitor, while the film coverage was about 50% with the conventional inhibitor.

These results are in a good agreement with the corrosion weight loss results showing greatly improved performance under the test conditions of the new water dispersible corrosion inhibitor.

The film persistency test was also performed in the sparged beaker test. The electrochemical (LPR) method was used to monitor the corrosion rate. The results are shown in Figure 2. The initial corrosion rate for the water dispersible corrosion inhibitor was 0.008 mm/yr (0.3 mpy) while for the oil soluble inhibitor corrosion rate was 0.025 mm/yr (1.0 mpy). After the first time replacement of the test fluid , the corrosion rate in the presence of water dispersible corrosion inhibitor was 0.043 mm/yr (1.7 mpy) while in the presence of the oil soluble inhibitor the corrosion rate was 0.139 mm/yr (5.5 mpy). After the second time replacement of the test solution, the corrosion rate for water dispersible corrosion inhibitor was 0.096 mm/yr (3.8 mpy) while for oil soluble inhibitor was 0.322 mm/yr (12.7 mpy). The results showed that the new corrosion inhibitor had lower corrosion rates and better film persistence and than the conventional oil soluble inhibitor.

In order to study the inhibitor performance at a higher temperature, the corrosion inhibition performance of the two inhibitors was evaluated in the wheel bomb system at 104 °C, with charging of 14.7 psi (101.3 kPa) CO_2 pressure at ambient temperature. The results are shown in Table 2. It can be seen that the new corrosion inhibitor is comparable or slightly better than the conventional oil soluble corrosion inhibitor at this temperature.

Partitioning Test

The partitioning of inhibitor into the water phase was determined indirectly by the copper ion displacement test. Due to the amphiphilic nature and high oil solubility of the test corrosion inhibitors, they partitioned between the oil and water phases with higher affinity towards the former. The effectiveness of the corrosion inhibitors depending on their partitioning into the water phase was evidenced by the results shown in Figure 3. It can be seen that film coverage is approximately over 90% with the new water dispersible inhibitor, while the film coverage is about 50% with the conventional oil soluble inhibitor. Therefore, the new water dispersible corrosion inhibitor partitioned better into the aqueous phase, giving a better film coverage than the conventional oil soluble corrosion inhibitor.

Dispersibility Test

Dispersibility of inhibitors in water was further investigated. The dispersion in NACE brine/Isopar M mixture was shown in Figure 4. It can be seen that new corrosion inhibitor showed much more turbid dispersion in brine than that of oil soluble corrosion inhibitor. Microphotographs of dispersed particles in brine under a microscope was shown in Figures 5 and 6. It can be seen that the oil soluble corrosion inhibitor dispersed in brine produced large spherical emulsion droplets (aggregates) of approximately 100 microns in diameter (Figure 5). For comparison, much smaller individual droplets (~ 1-2 microns) were observed for new water dispersible corrosion inhibitor (Figure 6).

It is well known that highly water dispersible corrosion inhibitors perform better than more soluble inhibitors in batch type of applications.[4, 5] However, the importance of the size and distribution of the dispersion in brine is much less well understood. The smaller the droplets the more stable the dispersion and more effective the film forming ability of the inhibitor. The persistence of turbid solution of the new water dispersible corrosion inhibitor may suggest the presence of lamellar bilayer structure formed in solution that could promote more stable admicelle bilayer on metal surface.[6-8] Hence, this highly dispersible new corrosion inhibitor contributes to better performance of corrosion inhibition than the conventional oil soluble corrosion inhibitor.

Emulsion Tendency Test

The emulsion tendency was investigated to see if the high dispersibility of inhibitor can cause the emulsion problem. The model oil (Isopar M) and brine (NACE brine) were used initially in the lab. The results were shown in Table 3. The results showed that the new corrosion inhibitor has similar emulsion separation time with the oil soluble corrosion inhibitor. The emulsion tendency with the actual field fluid from East Texas was also performed, and the new corrosion inhibitor showed the same emulsion tendency as of the current inhibitor (Table 4).

Field Trial

In order to validate the lab results obtained with the new water dispersible product, a field trial was initiated for several rod pumped wells in East Texas. These wells averaged about 3,600 feet in depth with 2.041 inch inside diameter tubing. The bottom hole temperature is 150 °F (65.6 °C) and field brine is 50,000 TDS with compositions of 37,000 ppm chlorides, 400 ppm bicarbonates, 2,800ppm calcium, 212 ppm barium, 1-5 ppm sulfates. The well produces 3 bbl of oil and 375 bbl of water per day with a small amount of H_2S (2 ppm) and CO_2 (0.4%). A typical treatment program consisted of batch treating with 5 gallons (18.9 liters) of incumbent oil soluble corrosion inhibitor every other week into the well and flushed down the annulus with 3 barrels of produced water. The higher fluid levels made it increasingly more difficult to flush the oil soluble corrosion inhibitor through the fluid level and to the pump.

The newly developed water dispersible corrosion inhibitor was tested in these high fluid level wells using the same dosage rate and flushing with the incumbent inhibitor. The results are shown in Figure 7. The iron counts were used to monitor corrosion rates twice a week dropped from an average of 6.2 ppm to 3.8 ppm immediately after the first treatment. The ion count was converted to general corrosion rate based on flow rate, tubing diameter and length. Once the stable low iron counts readings were established, the treatment rate was reduced over the course of 4 months to 4 gallons (15.1 liters)and 3 gallons (11.3 liters)/2 weeks. At a treatment rate of 3 gallons (11.3 liters)/2 weeks the average iron counts of 4.9 ppm was still lower than that of incumbent at 5 gallons (18.9 liters)/2 weeks. This corresponds to a 21% reduction in iron counts and a 40% reduction in chemical treatment volume. Hence, the new water dispersible corrosion inhibitor showed improvement in overall performance over the conventional oil soluble inhibitors at a significantly lower dosage rate in batch applications

CONCLUSIONS

The new water dispersible corrosion inhibitor showed higher performance, better dispersibility/partitioning and enhanced film persistency compared to the conventional oil soluble inhibitor in batch treatment applications. The performance of the new corrosion inhibitor is enhanced by using the proprietary dispersion technology. The corrosion inhibition and film coverage test performed on the new corrosion inhibitor demonstrated better corrosion inhibition performance than that of the conventional oil soluble corrosion inhibitor in the laboratory test. The field tests showed the same trend as of the laboratory test.

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Table 1
Film Persistency Test of Corrosion Inhibitor in Wheel Test *
(60 °C, P_{CO2} =14.7 psi (101.3 kPa), W/O ratio =90/10, changed fluid twice, 16 hours test)

Inhibitor	Concentration (ppm)	Corrosion rate, MPY (mm/yr)	% Protection
Blank	0	26.8 (0.680)	0
Conventional oil soluble inhibitor	5,000	15.0 (0.381)	44
New water dispersible corrosion inhibitor	5,000	0.2 (0.005)	99

* The experimental error is within 2%.

Table 2
Corrosion Inhibition Performance in Wheel Bomb Test *
(104 °C, W/O ratio = 90/10, charged 14.7 psi (101.3 kPa) CO_2 at 25 °C, 24 hours test)

Inhibitor	Concentration (ppm)	Corrosion rate, MPY (mm/yr)	% Protection
Blank	0	180.0 (4.569)	0
Conventional oil soluble inhibitor	5,000	9.1 (0.231)	80.8
New water dispersible corrosion inhibitor	5,000	8.4 (0.213)	82.3

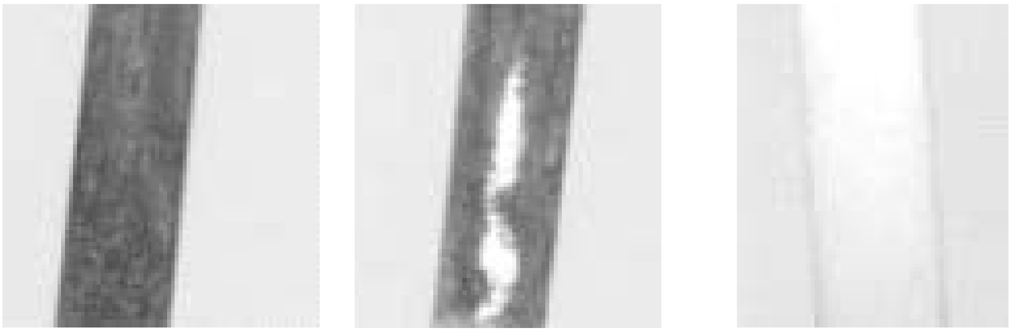
* The experimental error is within 2%.

Table 3
Emulsion Tendency Test of Corrosion Inhibitor at Isopar M/NACE brine, 10/90
(5,000 ppm, 20 minutes)

	Water	Oil	Oil-Water Interface Pad
Conventional oil soluble inhibitor	89	9	2
New water dispersible corrosion inhibitor	89	9	2

Table 4
Emulsion Tendency Test of Corrosion Inhibitor with field fluid
(oil/brine 1/99, 5,000 ppm inhibitor, 20 minutes)

	Water	Oil	Oil-Water Interface Pad
Conventional oil soluble inhibitor	98.9	0.9	0.2
New water dispersible corrosion inhibitor	98.9	0.9	0.2



Blank

Oil soluble inhibitor A

Water dispersible Inhibitor B

Figure 1 - Copper ion displacement test of corrosion inhibitors after rinsing with fluid twice (initial 5,000ppm inhibitor in Isopar M/NACE brine, 10/90, 60 °C for 16 hours).

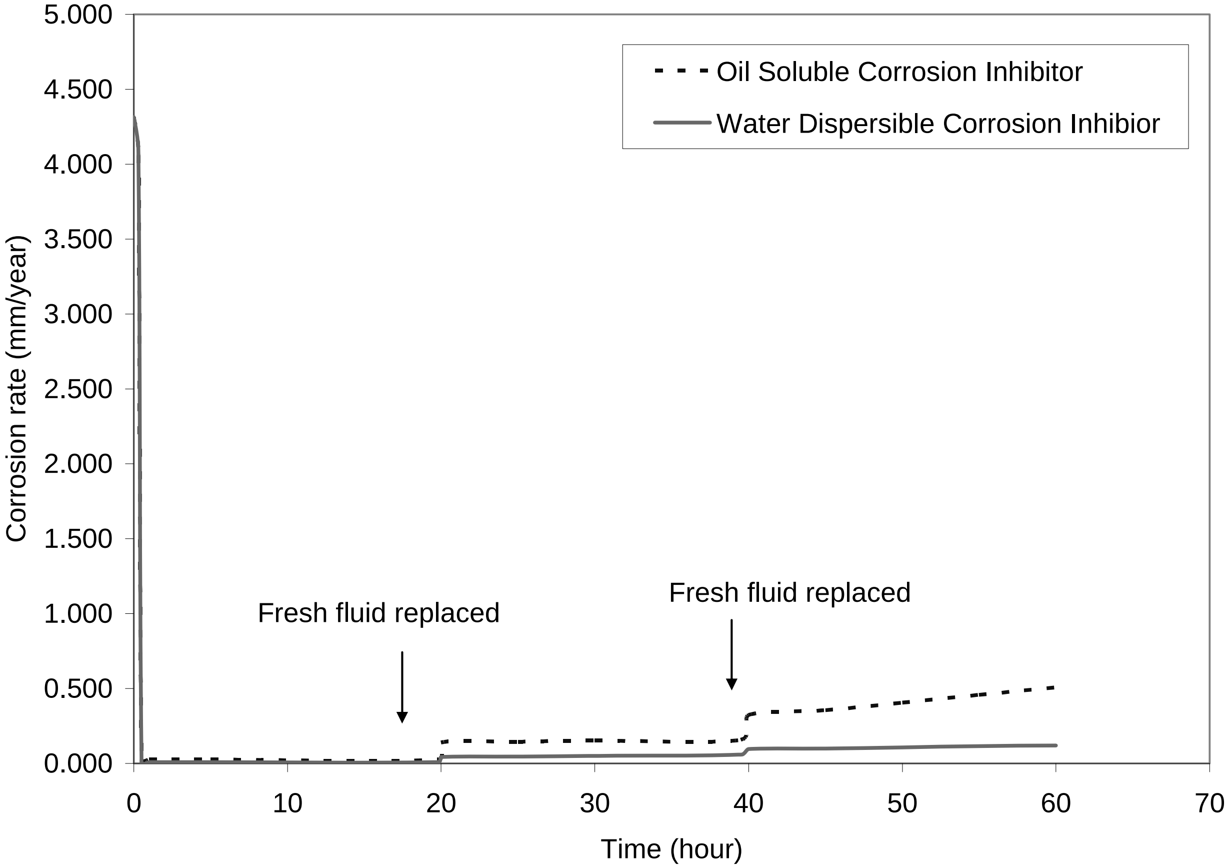
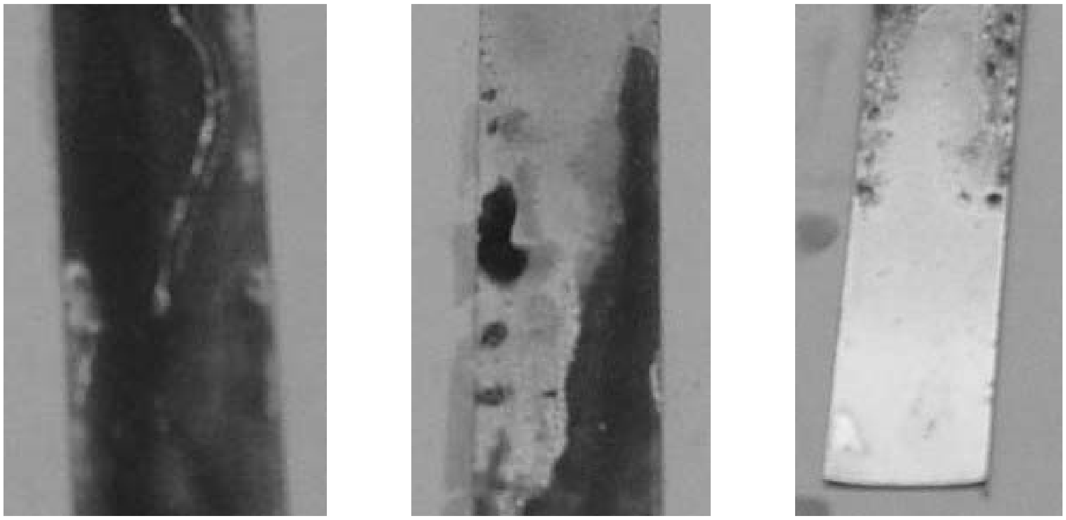


Figure 2 - Film persistency test of corrosion inhibitors in the sparged beaker test by LPR method (5,000 ppm inhibitor, 60 °C, CO_2 sparged, Isopar M/NACE brine, 10/90, fluid changed every 20 hours).



Blank

Oil Soluble Inhibitor A

Water Dispersible

Figure 3 - Copper ion displacement test of corrosion inhibitors from 500 ppm inhibitor partition into water phase (Isopar M/NACE brine, 10/90, 60 °C for 3 hours).

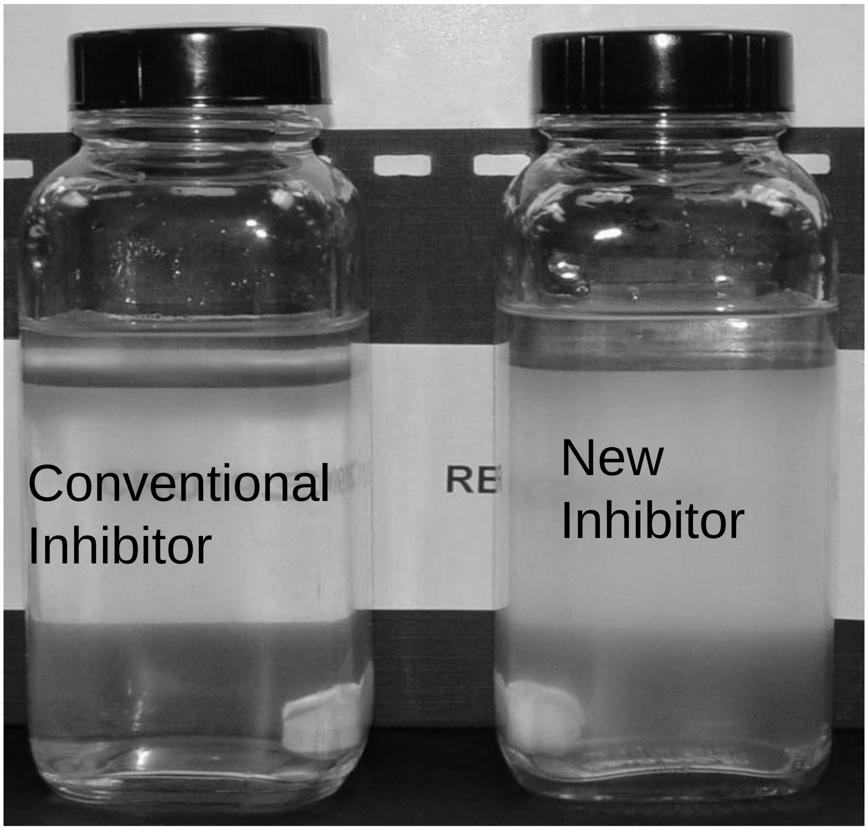


Figure 4 - Dispersibility of corrosion inhibitors after 1 hr of mixing.
(2,000 ppm inhibitor in CO_2 saturated solution, Isopar M/NACE brine, 10/90).

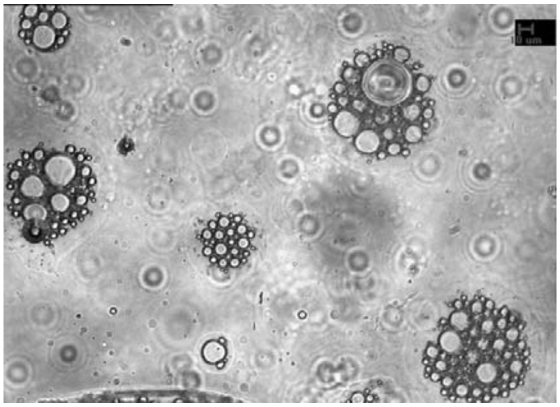


Figure 5 - Dispersion of oil soluble corrosion inhibitor in CO_2 saturated NACE brine.

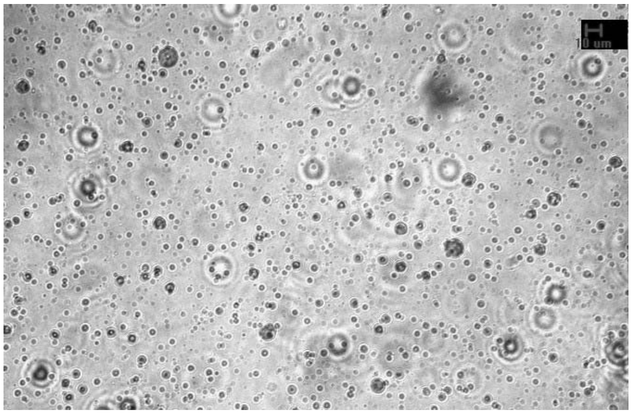


Figure 6. Dispersion of water dispersible corrosion inhibitor in CO_2 saturated NACE brine.

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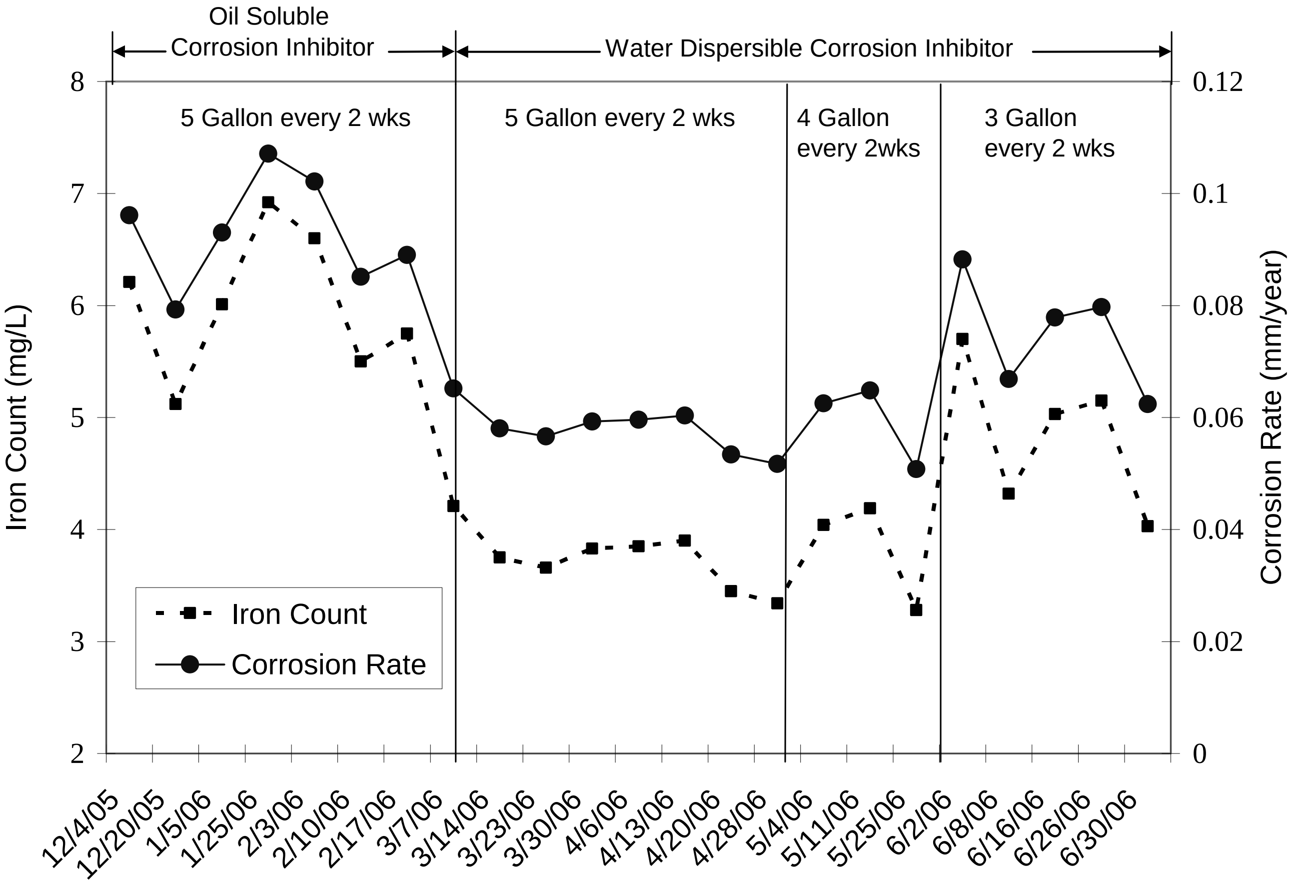

Figure 7 - Results of field test for new corrosion inhibitor in an East Texas oil well.