Paper No.
11093

NACE INTERNATIONAL CORROSION 2011 CONFERENCE & EXPO

DEVELOPMENT OF NEW CORROSION INHIBITOR TO PREVENT BLACK POWDER FORMATION USING QUARTZ CRYSTAL MICROBALANCE TECHNIQUE

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ABSTRACT

Black powder formation is an oxidative corrosion process that over time can cause operational problems as the solids collect within the system. There is a net weight gain within the system as molecular oxygen becomes incorporated as part of the solid materials. A novel quartz crystal microbalance (QCM) test apparatus has been developed to determine the effectiveness of various corrosion inhibitors to prevent black powder formation in sales gas pipelines. The QCM measures minute changes in frequency of a quartz crystal with weight gain/loss. For our test apparatus, the QCM crystal was coated with iron where small increases in mass due to oxidation of the iron layer are recorded as a drop in frequency. Using the Sauerbrey equation, the drop in frequency observed during corrosion testing can be converted to a corrosion rate. Several inhibitor chemistries were tested using the QCM apparatus. In this study it was found that a new oil-soluble corrosion inhibitor is the most effective for preventing black powder formation under the sales gas conditions.

Keywords: Black powder, corrosion testing, carbon dioxide corrosion, oxygen corrosion, corrosion inhibition, QCM

INTRODUCTION

Black powder is a term used to describe the grayish material generated in sales gas pipelines mainly as a result of internal corrosion of the pipeline wall.[1] It occurs in a variety of environments involving moist gas containing oxygen, hydrogen sulfide, and carbon dioxide.[2] In the presence of condensed water, 0.01 mole % oxygen content has been shown to have little effect on steel corrosion rates. Higher corrosion rates have been observed when the oxygen concentration reaches as high as 0.1 mole percent. Due to the perceived absence of water in “dry” pipelines, internal corrosion is generally not considered a main cause of black powder formation.[3] Several reports in the literature list black powder as being primarily iron oxides and hydroxides such as Fe_3O_4 and FeOOH.[3]

The hematite (Fe_2O_3) form of iron oxide often forms when water that is present in the system is saturated with dissolved oxygen.[3,4] The formation of black powder has been attributed to relatively insignificant chemical phenomena, i.e. very low corrosion rates occurring over large steel surface areas leading to large quantities of corrosion products (i.e., black powder).[5]

The main strategies for controlling black powder formation in sales gas lines are gas dehydration and mechanical removal (i.e., pigging) of the solid formed. In this paper a new black powder mitigation strategy is proposed using batch corrosion inhibitors that are effective in the presence of oxygen. In a previous paper we described the development of a novel corrosion test method, based on weight gain rather than weight loss, using the QCM technique. This QCM method allows corrosion inhibition measurements to be made under sales gas conditions.[6] In this paper, development of a new corrosion inhibitor for gas transmission lines using the QCM is reported.

For an inhibitor to be effective for batch applications, it should be readily soluble in diesel and have an appropriate viscosity. A low viscosity would lead to migration of the inhibitor to the bottom, 6 o’clock position of the pipe and provide incomplete coverage. To measure the effectiveness of different batch corrosion inhibitors, inhibitors were dissolved in diesel with a ratio of 10:1, diesel to inhibitor. This was done to as closely as possible simulate the batch application of inhibitors in the field. The performance of batch corrosion inhibitors was further studied at different concentrations and film thicknesses.

EXPERIMENTAL

Inhibitor Solutions

The work presented here builds upon our previous development of new batch corrosion inhibitors for gas transmission lines where the standard weight loss measurements of metal coupon testing was used.[6,9] Table 1 lists the four inhibitors tested and their basic chemistries. To minimize the number of variables, all tests were carried out using the following gas composition: CO_2 (16 psi), O_2 (0.2 psi), H_2S (0.002 psi), N_2 (83.8 psi). In order to deliver the desired concentrations of nitrogen, carbon dioxide, oxygen, and hydrogen sulfide, a gas delivery system consisting of thermal based mass flow controllers and control box was constructed.[6,7]

Table 1
Inhibitors Tested and Their Basic Chemistry

Inhibitor	Chemistry	Solubility
CI A	Proprietary ester	Oil
CI B	Phosphate ester	Oil
CI C	Amidoimidazoline	Oil
CI D	Fatty acid	Water

The corrosion inhibitors were first tested for their compatibility with diesel or water at various ratios. For the oil-soluble inhibitors (CI A, CI B, and CI C) the diesel/inhibitor ratios were varied from 4:1 to 10:1, diesel to inhibitor. The diesel used in this study contained a sulfur content of 0.041% (w/w). All three of the inhibitors were completely soluble in diesel at concentrations as high as 4:1 with no visible incompatibility. As mentioned above, initial testing for an inhibitor was carried out at a diesel to inhibitor ratio of 10:1. The water-soluble inhibitor (CI D) was dissolved in water in a ratio of 10:1, water to inhibitor. The CI D inhibitor was completely soluble in water at this concentration.

Viscosity measurements

Viscosity of inhibitor solutions in diesel was measured using a TA Instruments® ARG2 controlled strain rheometer. The viscosities were measured with a 10:1 diesel to inhibitor ratio. The diesel/inhibitor solutions tested had a viscosity of 3.8 cp. This value is close to the desired viscosity of approximately 3.6 cp.

Inhibitor Film Application

The application of a controlled amount of corrosion inhibitor proved difficult in that the deposition of larger quantities of inhibitor on the surface of the QCM crystal had the tendency to cause the QCM to lose the electrical signal. This is due to the inhibitor diesel solution seeping under the lip of the cool drawer and severing the electrical contact with the front side of the QCM. However, if not enough inhibitor is applied to the surface of the crystal, this will result in non-uniform coverage of the crystal by the inhibitor and little or no corrosion inhibition will be observed. These two factors, loss of signal and non-uniform coverage, had to be taken into account when applying the inhibitor to the iron-coated surface. The optimum amount of inhibitor/diesel applied to the crystal monitored via frequency drop in the QCM was found to be 0.5 μL.

The application of the corrosion inhibitor to the crystal was performed with the probe assembly outside of the main Hastelloy vessel. The cool drawer assembly was removed from the probe and, using a Hamilton® 10 microliter syringe, 0.5 μL of liquid was applied to the crystal surface. Figure 1 shows an image of (a) the inhibitor diesel mixture being applied to the iron-coated crystal surface via a microliter syringe (darker area in the center), and (b) an image of the iron-coated crystal in the cool drawer assembly coated with a diesel/inhibitor layer. After the application of the inhibitor, the cool drawer with the crystal was placed back in the probe assembly and a frequency drop of approximately 5000 Hz was observed. This corresponded to a total diesel/inhibitor film thickness on the order of 1 μm, which is thinner than the typical 3 to 5 μm inhibitor film thickness obtained using the standard "dip and drip" procedure.[9]

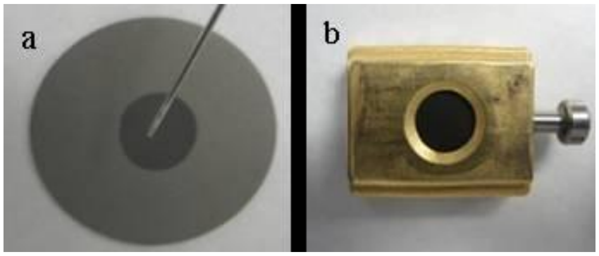

Figure 1: (a) Micro liter syringe used to apply a 0.50 µL drop of inhibitor solution to the iron-coated crystal surface, (b) crystal with inhibitor film placed in the cool drawer assembly

Figure 2 shows a typical frequency plot before and after the application of the inhibitor to the iron-coated crystal, and the corresponding drop in frequency. In this case, the baseline frequency of the iron coated-crystal was ~5,935,790 Hz. The frequency of the iron coated crystal is measured extremely accurately to a factor of 5 Hz. Frequency measurements change with pressure, viscosity of gas, and temperature. Our experiments are carefully constructed to keep these factors constant during the experiment. An increase in frequency of 48,258 Hz occurs whan a 1 µM thick iron film is deposited on a gold coated quartz crystal. The crystal was then taken out and the inhibitor was applied to the crystal surface (~3 min break in the frequency–time curve). The frequency of this crystal was again measured, after being inserted in the cool drawer assembly. As can be seen in Figure 2, the initial baseline frequency of the crystal in air (blank) was followed by a significant drop (~5000 Hz) with the inhibitor film deposited. Due to dampening of the intrinsic vibration of the quartz crystal by the inhibitor film, the corresponding increase in mass of the crystal translates into a decrease in frequency.[6,7] Once the frequency stabilized, indicating the presence of a uniform inhibitor film, the iron-coated crystal with the inhibitor film was then placed in the vessel for testing as shown in Figure 3.

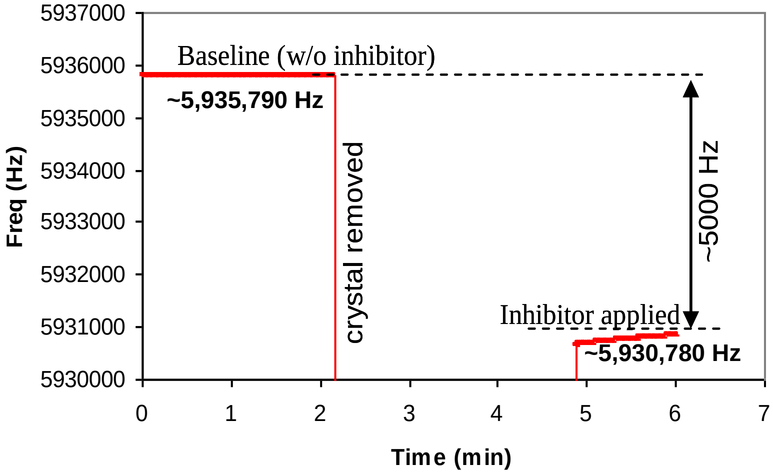

Figure 2: Frequency vs. time plot for inhibitor film applied to iron-coated crystal

RESULTS AND DISCUSSION

Corrosion Rate Measurements

The method for forming an aqueous layer was modified slightly from our previous studies using a "step-wise" gas addition procedure. Figure 3 shows a typical frequency versus time plot for an iron-coated crystal with an effective corrosion inhibitor, with each step being numbered.

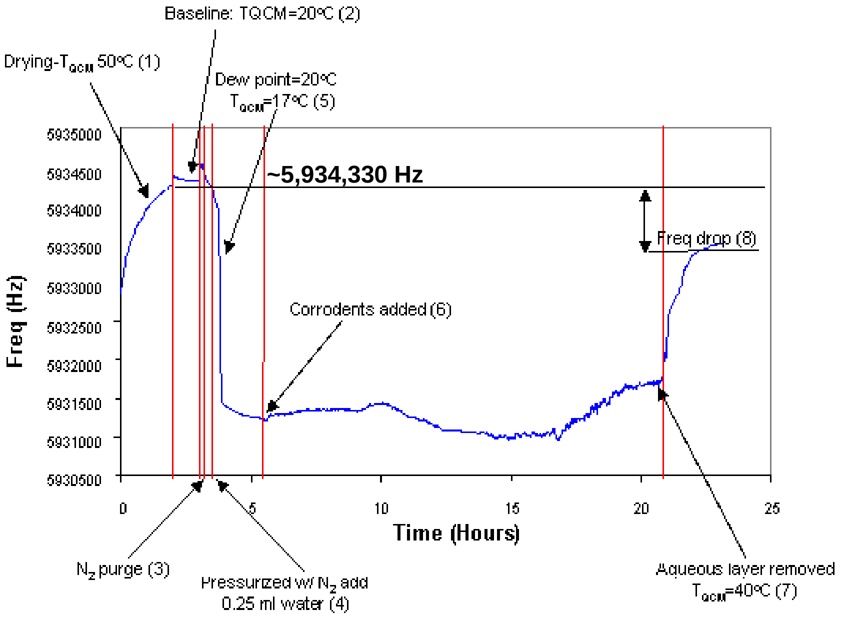

Figure 3: Frequency vs. time plot for stepwise addition of acid gases for corrosion inhibitor CI A

Prior to each run, the vessel is purged with nitrogen for five minutes at 10 L/min to remove any oxygen or excess moisture in the vessel. The initial step (step 1) is a drying step to remove excess diesel from the diesel/inhibitor mixture applied via the above-mentioned inhibitor film formation procedure. The drying step is done to establish a "steady state" baseline condition as a point of comparison for frequency drop determination. With an excess of diesel on the iron surface, little or no condensation will take place due to water and diesel being immiscible; therefore, the excess diesel had to be removed in order to form a stable aqueous condensation layer on the iron surface. Excess diesel was removed by setting the temperature of the quartz crystal (T_{QCM}) to 50ºC after it had been loaded in the vessel. This dries the crystal in addition to the five-minute nitrogen purge at the beginning of each run prior to the start data collection. The drying step at T_{QCM} = 50°C was done for two hours under 100 psi nitrogen. After the nitrogen purge and drying step, approximately ~3500 Hz (5,934,330 to 5,930,780 Hz) (Figures 2 and 3) or ~70% of diesel was removed from the surface of the crystal. As material is being removed from the surface of the crystal, as will be discussed, these drying steps are recorded as an increase in frequency. During the drying step, diesel is being removed from the crystal surface, and thus the weight is decreasing. Since there is less weight on the surface of the crystal, there is less dampening of the vibration of the quartz crystal, and the decrease in weight is observed as an increase in frequency.[6,7]

As discussed in a previous paper, reproducibility was a serious challenge in drying the crystal. However, for the concentration study discussed later, as with the run depicted in Figures 2 and 3, the nitrogen purge and drying step resulted in a frequency loss on the order of ~3500 Hz. (5,934,330 to 5,930,780 Hz). This results in an inhibitor/scavenger film on the iron surface that is approximately ~1500 Hz (5,935,790 to 5,934,330 Hz) “thick”, which is recorded as a net frequency drop, or ~1/3 of the original thickness (0.3µm). As a result of the nitrogen purge/drying step and the removed diesel, the concentration of the inhibitor is much higher than the initial application, while the amount of inhibitor in the film remained the same. With a 10:1 diesel to inhibitor ratio, after the drying step, the resulting diesel to inhibitor ratio would be between 5:1 and 2:1. Once the drying step was completed, a one-hour baseline was maintained at 20ºC (step 2), this served as the previously mentioned “steady state” baseline point of comparison after the test to measure the frequency drop and subsequent corrosion rate. Following acquisition of the baseline, step 3 is an additional short nitrogen purge, which was performed to remove any residual moisture, oxygen, or volatized diesel from the vessel. Next, the vessel was pressurized with the calculated partial pressure of N_2 (83.8 psi). During the pressurization with N_2, 0.25 ml of water was injected into the vessel, indicated in step 4. Once the dew point of inside the vessel reached 20ºC, the T_{QCM} was set to 17ºC (step 5), which initiated the formation of the aqueous condensation layer on the crystal surface. After the condensation layer had formed and was stable for approximately two hours, the corrosive gases were added at the following partial pressures: CO_2 (16 psi), O_2 (0.2 psi), H_2S (0.002 psi). The test was then allowed to run overnight, as seen in step 6. After approximately 16 hours, the condensation layer was removed by setting the T_{QCM} to 40ºC(step 7). To determine the total frequency drop (step 8), the frequency was allowed to stabilize, and was compared to the baseline observed in step 2. Methods to convert the frequency drop to the corrosion rate are described in a previous paper.[7] It is assumed that after deposition of the inhibitor and the drying step, there is a uniform inhibitor layer on the surface of the crystal. However, as will be discussed, this may not be the case. There are potential gaps within the film that allow for corrosive gases to permeate the film, and, even with an effective inhibitor such as CI A, cause some corrosion.

Figure 4 shows the frequency versus time plot for a partially/less effective inhibitor. The two main differences from the effective inhibitor shown in Figure 3 is that 1) there is a drop in frequency after the addition of corrosive gases, indicative of weight gain due to corrosion, and 2) there is a significantly higher frequency drop at the end of the test, due to weight gain from corrosion. The higher the mass gain of the crystal, the greater the frequency drop.

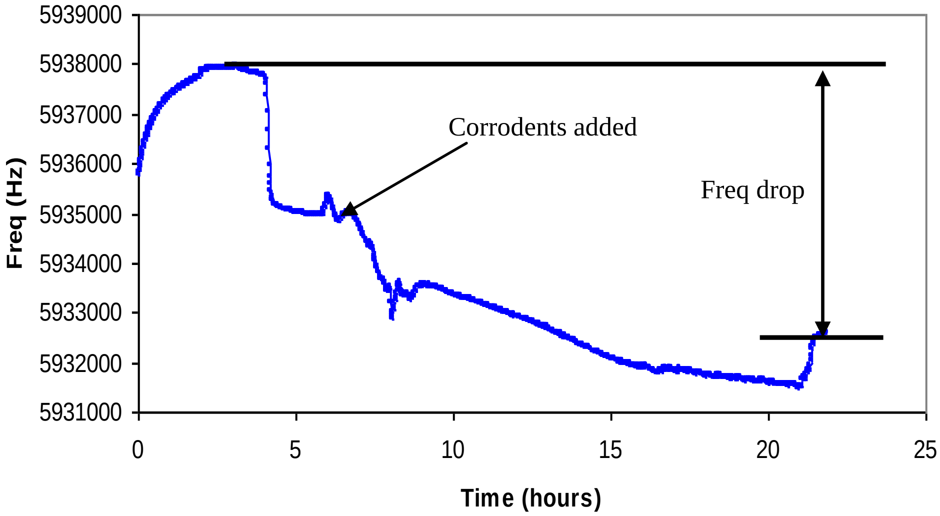

Figure 4: Frequency vs. time plot for stepwise addition of acid gases for less effective corrosion inhibitor (CI D)

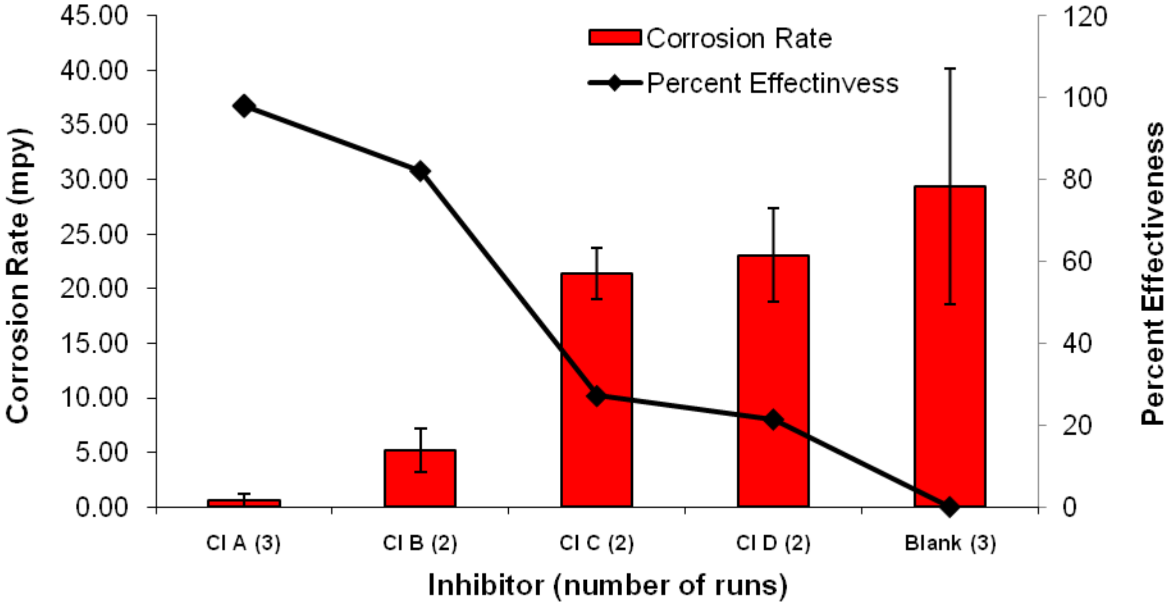

Figure 5: Corrosion rates and percent inhibition for inhibitors

As can be seen in Figure 5, the new inhibitor, CI A, provided the most effective corrosion inhibition and lowest observed corrosion rate. The inhibitor CI B provided effective corrosion inhibition, although was not as effective as CI A. This confirms the findings from the previous work, whereby CI A provided the most effective corrosion inhibition with standard metal coupon testing, measured with weight loss and visual observation.[9]

As mentioned above, visual inspection of the iron-coated crystals was used, in addition to frequency drop/corrosion rate measurements, as an indicator of corrosion inhibitor/scavenger performance. Table 2 shows images of crystals and the testing condition.

Table 2:
Images of Crystals and Testing Conditions

Testing Condition	**Image**	**Testing Condition**	**Image**
(1) pre-corroded prior to testing		(4) CI B, partially effective inhibitor	
(2) blank, no inhibitor		(5) CI C, ineffective inhibitor	
(3) CI A, effective inhibitor		(6) CI D, ineffective inhibitor	

In a previous paper, it was discussed that there is a pre-corrosion step performed on the crystals prior to testing (image 1), that leaves a dark silver gray layer on the surface.[6,7] This crystal serves as a point of comparison for visual inspection of corrosion inhibitor effectiveness. Image 2 shows a crystal after testing with no inhibitor film being applied, with the above-mentioned stepwise addition procedure. As can be seen from the image, there are significant dark black deposits on the active area of the crystal, with small reddish hues visible, indicative of Fe_2O_3 or FeOOH.[7] Image 3 is a crystal treated with CI A after testing. As the images show, while there are some black corroded areas on the surface of the crystal, the surface is mostly clean, with a dark silver gray color of the pre-corroded crystal. The dark black spots are likely the result of breaks within the inhibitor film at the perimeter of the film that allowed corrosive gases to reach the iron surface. However, due to the low frequency drop of the crystals treated with CI A (less than 1000 Hz), the oxidized areas are only superficial and do not degrade the integrity of the iron film. Image 4 is the result of testing with the inhibitor CI B, a partially effective inhibitor, showing some dark black deposits on the surface, certainly more than were present with the CI A. Crystals treated with the ineffective inhibitors CI C and CI D are shown in images 5 and 6 of Table 2. As can be seen, the images show significant dark deposits, indicative of corrosion. These images correspond with the results shown in Figure 5, showing CI C to be only 27% effective, and CI D being only 21% effective.

To better understand the effects of film thickness on the crystal, and to relate the inhibitor performance to field conditions, a detailed concentration study was carried out with the most effective inhibitor, CI A. For this study, CI A was dissolved in diesel at concentrations of 10, 5, 2, and 1%. Figure 6 shows the corrosion rate versus the percent concentration of CI A in diesel.

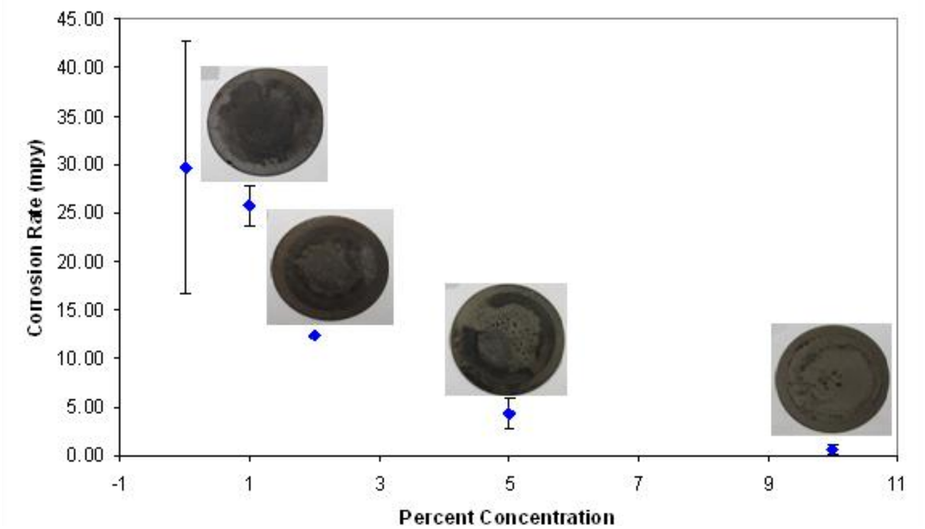

Figure 6: Corrosion rate vs. concentration of CI A in diesel

As discussed above, the drying step and nitrogen purge to remove excess diesel increases the concentration of the inhibitor during the test procedure, while the amount of inhibitor remained the same. For all CI A concentrations tested, the nitrogen purge and drying step resulted in a frequency loss of approximately 3500 Hz. This frequency drop corresponds to a loss of approximately 70% of the diesel during the nitrogen purge and drying step and results in a higher concentration of the CI A in diesel. Table 3 summarizes the initial and final concentrations and final film thickness after the nitrogen purge and drying.

Table 3
Initial and Final Concentrations of CI A in Diesel and Corresponding Film thickness

Initial Concentration%	~Final Concentration%	~Final Film Thickness µm
10	37	0.3
5	18	0.3
2	8	0.3
1	4	0.3

Since the main contribution to film thickness is due to the presence of diesel heavier fractions (after drying) the final film thickness measurements doesn’t directly relates to inhibitor performance. These values are given for illustrative purposes to show the typical film thickness of a batch corrosion inhibitor.

As can be seen in Figure 6, a 1% concentration shows essentially no inhibition, and only a very slight amount of inhibition observed at a 2% concentration. The most effective inhibition is observed at a 10% concentration, with a significant amount being observed at 5%. This is most likely due to a more complete coverage of the inhibitor over the iron surface, resulting in the prevention of corrosive gases permeating the iron film. As the images show, there are significantly more black deposits, presumably Fe_3O_4, as the inhibitor concentration is decreased. As the corrosion rate increases, the amount of black deposits on the surface of the crystal increases as well, in a non-uniform manner. CI A has proven to be an effective inhibitor in the above-mentioned prior testing with metal coupons[9] and in the QCM set-up. This finding is corroborated by the fact that even at the 10% concentration, little corrosion was observed, as shown in Table 2, with some localized corrosion indicative of a non-uniform coverage of the crystal surface.

CONCLUSIONS

The new QCM based test procedure was recently developed to evaluate batch corrosion inhibitors under the sales gas conditions. The apparatus is able to make accurate measurements of the slow process of black powder formation. Due to the process, we can effectively test chemical means of preventing black powder formation. A new oil-soluble corrosion inhibitor, CI A, was developed to prevent black powder formation in sales gas pipelines. Based on the measured corrosion rates and visual inspection of iron-coated crystals, CI A was shown to be most effective in inhibiting formation of black powder. CI B also provided some corrosion inhibition.

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