CHARACTERIZATION OF VOLATILE CORROSION INHIBITORS USING THE QUARTZ CRYSTAL MICROBALANCE AND SUPPORTING TECHNIQUES

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ABSTRACT

Corrosion inhibitors such as Volatile Corrosion Inhibitors (VCIs) and Contact Corrosion Inhibitors have become loosely ambiguous and differentiating between the two can become a gray area. For example, and the most common mistake is, classifying a material as a VCI when it is a contact inhibitor. Analytical techniques to qualify a material as a VCI have been investigated in order to clarify this ambiguity and to qualify the techniques and equipment for use in the determination of a VCI. The Quartz Crystal Microbalance (QCM) and an atmospheric corrosion monitor were used to characterize adsorption effects and corrosion monitoring of two commercially known inhibitors, sodium nitrite and dicyclohexylammonium nitrite on evaporated iron during atmospheric conditions.

Two devices will be used for in situ measurements of adsorption, QCM and an atmospheric corrosion monitor. During the adsorption process the QCM measures a frequency change that can be associated to a mass change due to adsorption of the inhibitor it is also capable of in situ monitoring corrosion rates of the substrate in a corrosive atmosphere. From experience and in theory the corrosion rate is expected to decrease due to the adsorption of the VCI. Which has been observed from in situ

measurements using the QCM.[3,6,7] The atmospheric corrosion monitor measures the resistance of oxides of a substrate due to corrosion in reference to a non corrosive element. It is tested here to measure its sensitivity in comparison to the QCM and to characterize its response during the adsorption of a VCI.

Key words: Quartz Crystal Microbalance, QCM, atmospheric corrosion monitor, sodium nitrite, dicyclohexylammonium nitrite, dichan, adsorption, Volatile Corrosion Inhibitor, VCI, contact corrosion inhibitor, detection devices.

INTRODUCTION

From the industrial, manufacturing and military point of view there is a common test performed on packaging materials which classifies a material as a suitable VCI carrier. It is a quick and relatively easy test that gives adequate macroscopic test results for packaging products. It is listed in the Federal Standards as Federal Standard 101c, Method 4031, Procedure B it is also commonly known as the Vapor Inhibiting Ability (VIA) test method. This is a test which uses a visual inspection to evaluate a polished 1018 steel surface for corrosion. The VCI material is usually impregnated into foam, paper, and films or even laminated onto the carrier. These methods are quite suitable for carrying the VCI which volatizes and absorbs onto the surface. In this test the metal sample is placed in a humidified chamber (approximately 1 liter) with the VCI carrier placed in the appropriate place. The steel sample is then visually inspected after 24 hours for signs of corrosion relative to a control sample.

This test is essentially the only test industrially that is used to classify a compound as a VCI. Under this test materials containing sodium nitrite, which is known as a contact inhibitor only, can not pass this test. Because sodium nitrite does not pass this test it was considered as a candidate for testing using the QCM and resistance measurement techniques. The QCM can detect a mass change of 10^{-9}g and has the capability of measuring adsorption of VCI compounds.[2,3,6,7]

The introduction of using the QCM for detecting adsorption effects and for monitoring the differences in corrosion due to the adsorption of a VCI is of recent interest.[2,3] The QCM in recent investigations appear to have some definite credibility in detecting the adsorption of a few VCIs. [2,3] It is a widely known fact that certain chemicals are very effective at emitting a vapor that can molecularly adsorb onto a metals surface. This molecular adsorption usually consists of a few monolayers and a few studies have been published on the adsorption of VCIs.[2,4,5]

The QCM method is based on the inverse piezoelectric effect, discovered by Jaques and Pierre Curie,[1] where an applied voltage to an ionic crystalline solid produces distortions, such as quartz. Piezoelectric materials have long been recognized as excellent indicators of mass changes because of the direct relationship between mass change and resonant frequency response. An equation developed by Sauerbrey in 1959 shows the linear relationship between deposited mass and frequency.[1]

$$\Delta f = -2.3 \times 10^6 f^2 \Delta m/A$$

This is the equation Sauerbrey used for an AT cut crystal vibrating in the thickness shear mode. Where AT is the special cut relative to the plane of the crystal to give it a zero temperature coefficient, Δf is the change in frequency, f is the resonant frequency given in MHz, and $\Delta m/a$ is the change in mass deposited on the crystal per unit area (g/cm^2).

The atmospheric corrosion monitor is a device that measures the resistance change in a specific metal as it corrodes with reference to a non corroding electrode. The sensor is made by evaporating the metal onto a glass substrate. A cable connects this closed loop electrode to a calibrated receiver. This sensor card is used in conjunction with the QCM for monitoring the atmospheric corrosion simulated in the cell.

EXPERIMENTAL

The 5 MHz AT cut quartz crystals used were supplied by Valpey-Fisher and are cut to have a zero temperature coefficient at 25 C. The crystals are then fitted with two key hole type electrodes by means of a Varian Electron Beam Evaporator. First a 500 Angstrom layer of titanium is evaporated onto the crystal followed with 1500 Angstroms of gold and last a 1500 Ang. of iron that is 99.9% pure.

Laboratory Equipment: The crystal was fitted into a probe made from Kel F® which was inserted into a customized 150 ml., 5 neck 2 gas inlets glass flask, designed by the author. The data acquisition was done using a IEEE connection from the power source and frequency oscillator to a computer.

The atmospheric corrosion monitor is the CK-3 from Rohrback Cosasco Systems. The sensor is a model 610-TF50-K00095 type D with a span of 2500 ± 10%. The resistance values are recorded by the monitoring instrument and stored in the recording computer. For corrosion rate calculations the following are given:

Span (Ang) x ∂Reading/1000 x 365/∂ time = Corrosion in Ang. per unit of time. **Eq. 1**

Where span is equal to one half of the deposited film thickness which in this case the span is 2500 Angstroms, and ∂Reading/1000 which is the change in the numerical dial reading of the monitor, it is divided by 1000 because it has 1000 scaled division points on the dial.

Set up: This is described elsewhere.[3]

Procedure: Each test for adsortion was carried out in the following fashion: First the sensor and the crystals were allowed to stabilize in flowing nitrogen followed with static nitrogen. Air was then introduced as a flowing gas then static from a cylinder of compressed air. This was done to identify any oxidation effects due to the different gasses.

After identifying a stable reading the first test of the system was to identify the characteristics of the two devices. This was accomplished by exposing the two sensors to a humidified atmosphere of air for a 24 hour period followed with dry air. This allows one to establish a reference threshold of sensitivity while at the same time measure for corrosion. Using dry air allowed for the identification of condensed water on the surface of the substrate.

The second step was to introduce the inhibitors to the cell one at a time. The inhibitors were introduced after the nitrogen and air stabilization time and monitored thereafter for as long as period as necessary to see any type of change in frequency or resistance change. If and after stabilization occurs a flow of dry air will be reinstated and the inhibitor withdrawn. This should aid, but not clearly define, in “partially” qualifying the inhibitor as a chemically adsorbed or physically adsorbed inhibitor.

Materials: The inhibitors used in this experiment were RG sodium nitrite supplied by Matheson Coleman & Bell Manufacturing Chemists and dicyclohexylammonium nitrite (DICHAN) mp. 139 C supplied by the Cortec Corporation.

RESULTS

Test one: In figure 1 the early and relatively flat part of the graph indicates no significant changes from nitrogen to compressed air. The first significant change in frequency, as recorded by the QCM, comes when humidified air is introduced. The resistance change, as measured by the corrosion monitor, is less than anticipated but still measures a small change. After the evaporation process the frequency again stabilizes and the resistance readings remained constant. The total frequency change on the evaporated iron without an inhibitor over a 24 hour time frame in humidified air appears to be 50 Hz and the resistance number was 0.6 units.

Test two. Refer to figure 2. The first part of the test followed the outline in the procedure using the nitrogen and air. This is seen by the relatively stable and flat plot. The plot remains virtually unchanged even after the introduction of the inhibitor. The oscillating frequency is the base background noise of the crystal. Introducing the flow of dry air at the end still does not effect either the QCM or the resistance probe measurements.

Test three. Refer to figure 3. The early part of the graph is constant and consistent with the earlier tests outlined. The change in frequency comes when the inhibitor dichan is introduced. There is a significant change in frequency (approximately 30 Hz) within a 24 hour period where it then seems to stabilize. A. Leng et al also indicate similar findings using a ammonium benzoate.[2] It remains stable for days after and shows no indication of evaporating at the end of the test when flowing dry air is introduced.

CONCLUSIONS

The QCM and the atmospheric corrosion monitor do not indicate significant change when switching from nitrogen to air. There is a measurable change observed in the frequency of the QCM and resistance measurements of the atmospheric corrosion monitor in a humidified atmosphere of air on evaporated iron. During the adsorption process the in situ readings of the QCM clearly indicate a change in frequency due to adsorption for the inhibitor dichan. The corresponding in situ atmospheric corrosion monitor measurements show no significant increase in resistance due to adsorption of either inhibitor. The atmospheric corrosion monitor appears to lack the sensitivity that the QCM is capable of for measuring adsorption of a VCI. The classification of sodium nitrite does not qualify as a VCI using these techniques. The inhibitor dichan shows clear significant indications that it can be considered a VCI, and very possibly a chemically absorbed inhibitor, using the QCM equipment and this technique.

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Figure 1

Figure 2
Figure 3