VCI'S FOR MITIGATING
ELECTRONIC CORROSION

By

Boris A. Miksic
Cortec Corporation
4119 White Bear Parkway
St. Paul, MN 55110

Paul Jaeger
Cortec Corporation
4119 White Bear Parkway
St. Paul, MN 55110

Christophe Chandler
Cortec Corporation
4119 White Bear Parkway
St. Paul, MN 55110

ABSTRACT

Sophisticated topside electronics aboard today's Navy ships are becoming evermore increasingly expensive to replace due to corrosion. This paper discusses a ship board experiment using a solvent based Volatile Corrosion Inhibitors (VCI) solution used to inhibit the corrosion of electrical parts due to ocean type corrosive atmospheres and testing with the Quartz Crystal Microbalance, QCM and an atmospheric corrosion monitor to support the ship board conclusions.

Keywords: Quartz Crystal Microbalance, atmospheric corrosion sensor, triazole, corrosion, inhibitor, resistance, oxide growth, frequency, solvent, mass change, volatile corrosion inhibitors, vapor phase inhibitors.

INTRODUCTION

As the world of electronic systems gets increasingly smaller so must the ability for corrosion protection to do the same. As the worlds technology gets more and more sophisticated it is a pleasant ordeal when there is information that can be presented where it couples the technology of today with practical applications. This is what was in mind as this study will come to show. Testing was conducted aboard an active Navy ship and laboratory testing was done to support the ship board testing.

The macroscopically applicable part of the experiment was conducted onboard an active Navy ship where a solvent based VCI solution was sprayed into electrical enclosures consisting of cable, wires, and connectors consisting of various metals. The inside of the enclosures were then sprayed once a month. The fixtures within the enclosures were then monitored by a visual inspection (slides to be presented at presentation), Universal Enterprises Digital Meter DM-310A for resistance, and a Navy standard 500 V Megger for leakage measurements.

The Quartz Crystal Microbalance was set up to monitor the mass change due to the growth of copper oxide. 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. Piezoelecric 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 was developed by Sauerbrey, in 1959[1], that showed a linear relationship between deposited mass and frequency changes.[1] For an AT cut quartz vibrating in the thickness shear mode the equation is

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

where Δf (Hz) is the change in resonant frequency, f is the resonant frequency (MHz) and $\Delta m/A$ is the mass deposited per unit area (g cm^{-2}).

The atmospheric corrosion monitor is a device that measures the resistance of the growing oxide layer in reference to a non corroding electrode on a closed loop sensor. This device can be installed to fit almost anywhere. It was incorporated with the QCM to give in situ resistance measurements in collecting laboratory data in an ocean type atmosphere.

EXPERIMENTAL

The AT cut quartz crystals used are 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 an Varian Electron Beam Evaporator. First a 500 Å layer of titanium is laid onto the crystal followed by 1500 Å layer of gold.

Preparation of the quartz crystal for electrodeposition of copper was done by a ultrasonic cleaning in a mild detergent followed with a 18 **M** de ionized (DI) water rinse, a 2-propanol rinse, a DI water rinse and finally dried with argon.

Laboratory Equipment: The crystal was then fitted into a probe of Kel F® which was inserted into a customized 115 ml., 3 neck 2 gas vent flask designed by the author. The solution used for copper electrodeposition is: 0.5M $CuSO_4$, 1.0 M H_2SO_4. Deposition was accomplished using a EG&G Model 174 Potentiastat at -200 mA over potential to a desired thickness of 2000Å.

After deposition the flask was then rinsed with DI water and dried with argon. The probe containing the crystal was then inserted back into the flask for exposure to the various atmospheres. The flask was fitted so that various gasses could be used to maintain controlled atmospheres. The frequency of the crystal is then monitored by the power source and frequency counter via IEEE connections to a computer for data collection.

The atmospheric corrosion monitor sensor was purchased from the Rohrback Cosasco Systems. The sensor has a deposited copper film thickness of 2500 Å. For corrosion rate calculation and metal loss the following are given:

$$\frac{.0304 \times \text{Span (Å)} \times \partial \text{Reading}}{\partial T \text{ (days)}} = (\text{Å/mo.}) \qquad \text{Eq. 1}$$

$$\frac{\text{Reading} \times \text{Span(Å)}}{1000} = \text{mass loss relative to 2500 Å} \qquad \text{Eq. 2}$$

Where .034=365 days/12 mo., Span=½ of the deposited film thickness

Set up: Refer to figure 1 for the details of the glass chamber used. The glass chamber was placed inside the Plexiglass box which was purged with dry nitrogen. The glass chamber is fitted with a gas inlet and outlet and two probes which can accommodate an inhibitor and a desiccant or other solids.

The ship board conditions consisted of a test panel with four common, commercially available, brass electrical boxes connected to a portable panel. The wiring consisted of a 'daisy chain' method to create multiple connections for resistance measurements. Each box was tested for continuity and the wires were meggered for leakage. The rubber gasket was removed from the cover plate and all initial electrical tests proved to be similar. Three boxes were treated with three different inhibitors and one box as a control.

Application Method: The method for application for the boxes on the ship was from an aerosol dispensed container. The crystal and atmospheric sensor were dip coated and left to air dry.

Materials: Inhibitor solution "A" is a proprietary blended, solvent based, VCI inhibitor, solution "B" and "C" are solvents containing inhibiting additives. The ocean water used in

the lab experiment conforms to ASTM D 1141 "Standard Specification for Substitute Ocean Water". The portable board with the electrical boxes was sprayed with ocean water at a frequency of once a month.

Procedure: The portable ship board testing incorporated 3 inhibitors "A", "B", and "C" which were sprayed into a respective electrical box. All 4 boxes were then sprayed with ocean water. The box covers then placed back on and another mist of ocean water was sprayed over the outside. The panel was then placed on the weather deck and given a southerly exposure. At one month intervals the boxes were checked for their particular measurements.

The laboratory testing consisted of purging the glass cell with dry air to establish a base line indication. This was followed with a humidified ocean air and then followed with dry air. The frequency change that is observed after the de-adsorption of the humidified air is then taken as the frequency change due to the corrosion of the substrate. The atmospheric sensor's reading is then entered into equation 1 to receive the corrosion rate.

RESULTS AND DISCUSSION

Figures 2 and 3 are the laboratory results which show the change in the copper surface when exposed to the humidified ocean type conditions. Figure 2 is the graph of the data showing the inhibited coated QCM and atmospheric sensor with inhibitor "A". Figure 3 is the graph of the data collected from a copper surface without an inhibitor present in humidified ocean conditions.

In Figure 2 the graph of the QCM shows a continuous increase in frequency, this frequency change could be due to the continuous evaporation of the solvent, the boiling point of the solvent is greater than 130 F. However, in interpreting the continuous increase in frequency this also indicates that there is no mass loading in the presence of a corrosive atmosphere. The graph of the corrosion monitor indicates a slight increase from the dial reading, in terms measuring corrosion and using Eq. 1 it equals 6-7 Å/mo.

In Figure 3 the QCM graph shows an initial decrease in frequency and the corrosion monitor graph indicates a slight increase in its reading. These changes are strongly suspected to be from the oxidation and vapor adsorption of the copper from the cylinder of compressed air. When the introduction of ocean humidified air is introduced into the chamber the graphs change significantly. The change in the graph of the QCM is due to the mass change from the adsorption of the vapor molecules with copper. The contact with this thin film then causes the oxidation and the corrosion of the copper surface. The corrosion effects of the copper are seen at the end of the graph after the desorption process is completed. The amount of corrosion as measured by the QCM can be seen as the difference between the initial frequency and the final frequency which indicates a increased mass. The corrosion as measured by the corrosion monitor is seen in the change of the readings. Using Eq. 1 gives the corrosion rate as 24-30 Å/mo.

The results from the portable panel shipboard tests are shown in Figures 4 and 5. In Figure 4 the control box and the box treated with inhibitor "A" and "B" show no increase in resistance measurements. The box sprayed with "C" did show an increase in resistance. In Figure 5 the graphs, as measured by the Megger, indicate no negative effects between the control and the box sprayed with inhibitor "A". The boxes sprayed with "B" and "C" show results ranging from 500K-20M units. Along with these measurements a visual inspection of the boxes was done and recorded by photographs*. In the photographs it can be seen that there was no signs of significant copper oxide on the electrical box protected with inhibitor "A". The visual inspection shows the failure of the control versus the spray inhibited boxes.

Note these test results are intermittent results and the time of year that the data was collected was between January and March of 1995.

CONCLUSIONS

The data collected by the QCM and the atmospheric corrosion monitor show a substantial indication that the amount of corrosion that occurs within the first 24 hours is a measurable amount. The detection ability, $10^-9 g/cm^2$, of the QCM has shown to be the best for measuring the sensitive mass changes due to the initial adsorption of water and consequently the initial corrosion of copper.

The atmospheric corrosion sensor is also a credible detector of showing the corrosion of copper by utilizing the resistance measurements of a deposited thin film of copper. The use of these instruments were incorporated to shed light on how quick and detectable corrosion is on the microscopic level and to correlate and support the results from the macroscopic field testing. The field testing showed the two "B" and "C" inhibitors to have suffered in the resistance, Megger, and the visual testing and that the control failed in the visual inspection. It is clear that the VCI blended solvent, "A" showed better performance in the micro and macroscopic worlds as seen in the graphs and to be seen in the photographs.

*Photographs to be presented at NACE 96 conference.

REFERENCES

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        Publisher: 1984, Kel F® Kel F is a registered Trade Mark of 3M.
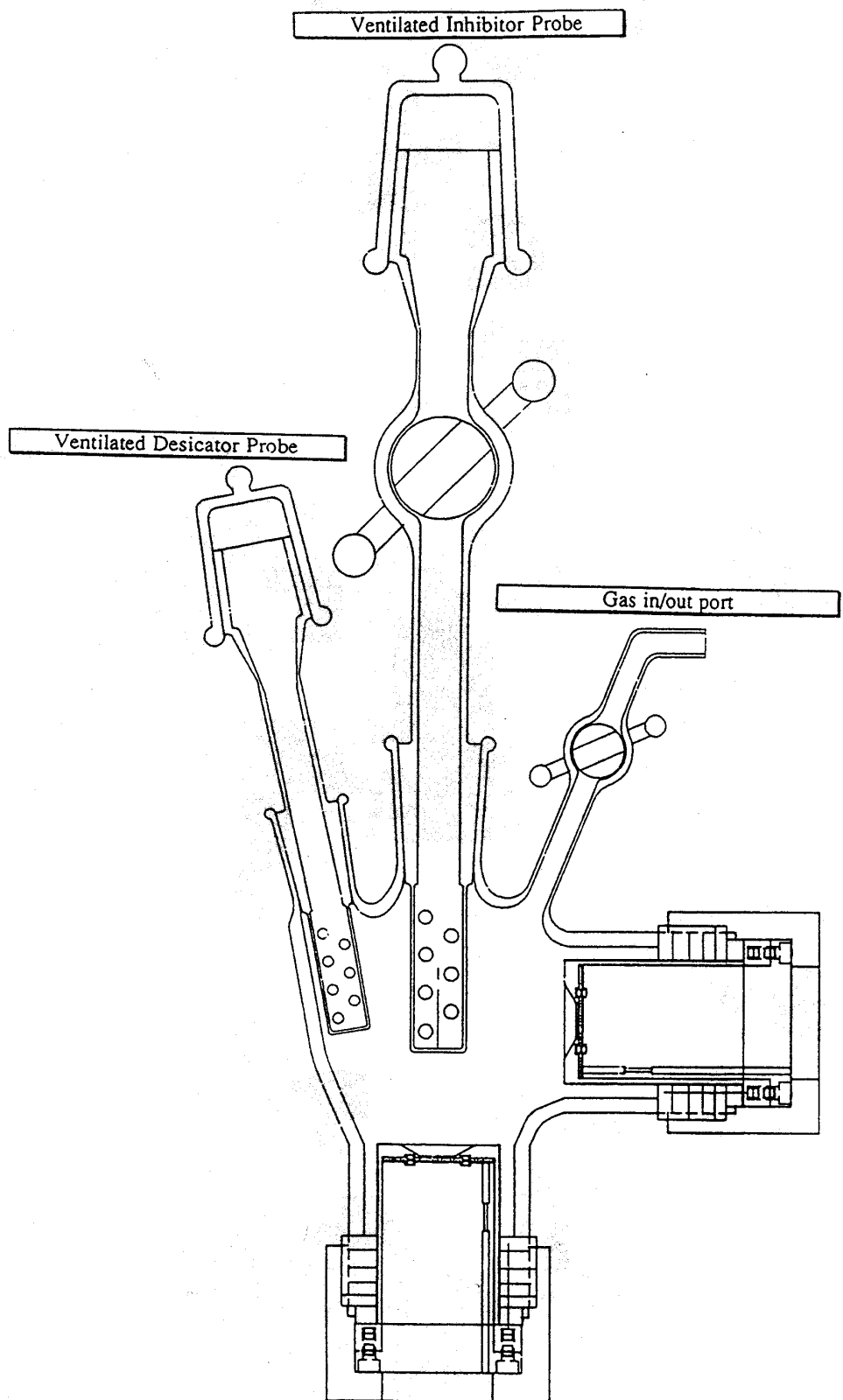
Figure 1 Glass Housing Apparatus for Corrosion Sensors. Used to Monitor the Corrosion of Synthesized Atmospheres
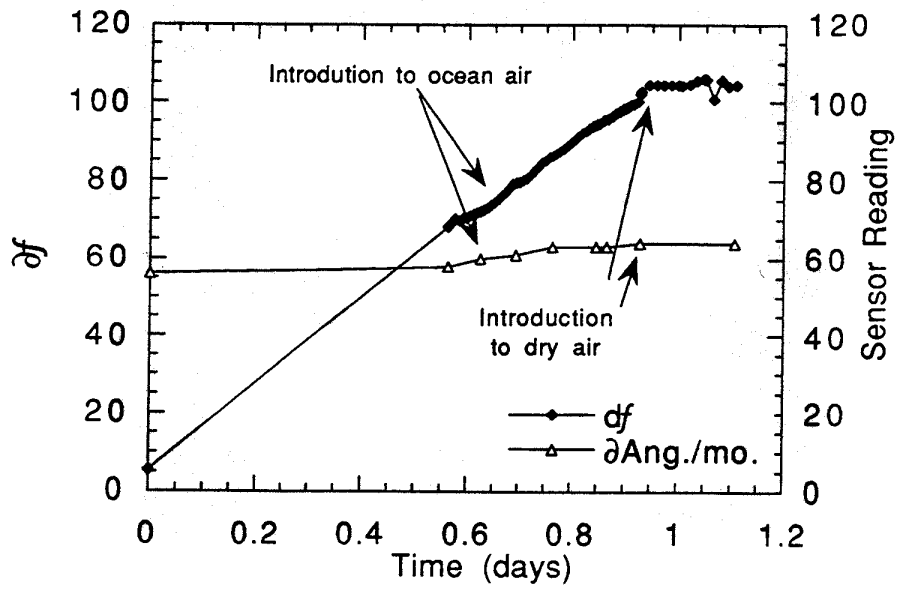
Figure 2 QCM and Corr. Monitor Readings in Synthetic Ocean Atmosphere with Inhibitor
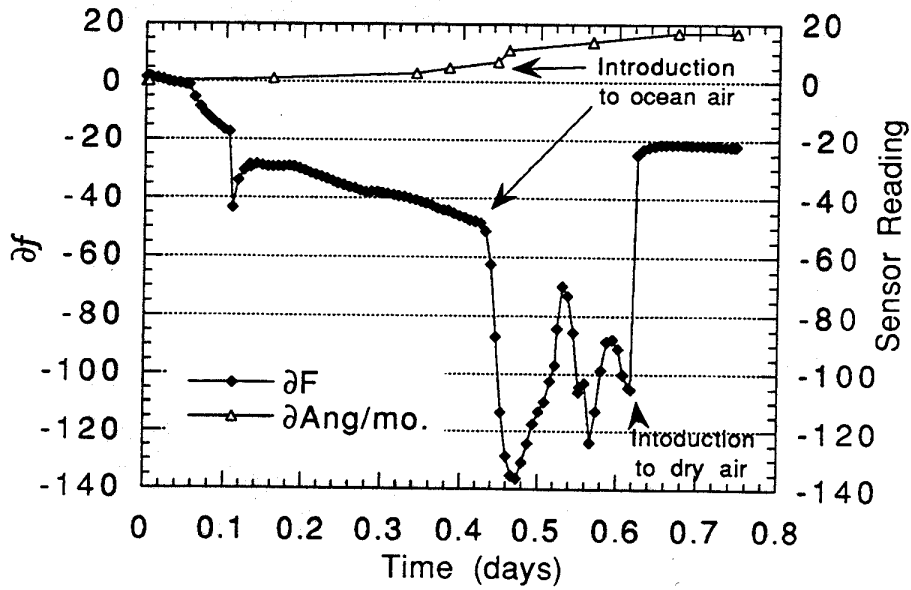

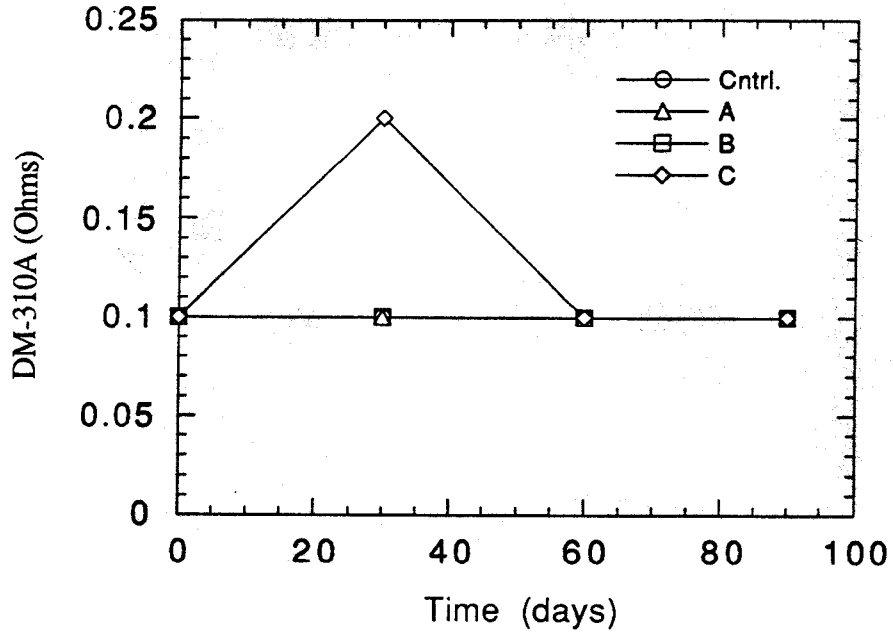Figure 3 QCM and Corr. Monitor Readings in Synthetic Ocean Atmosphere with out inhibitor

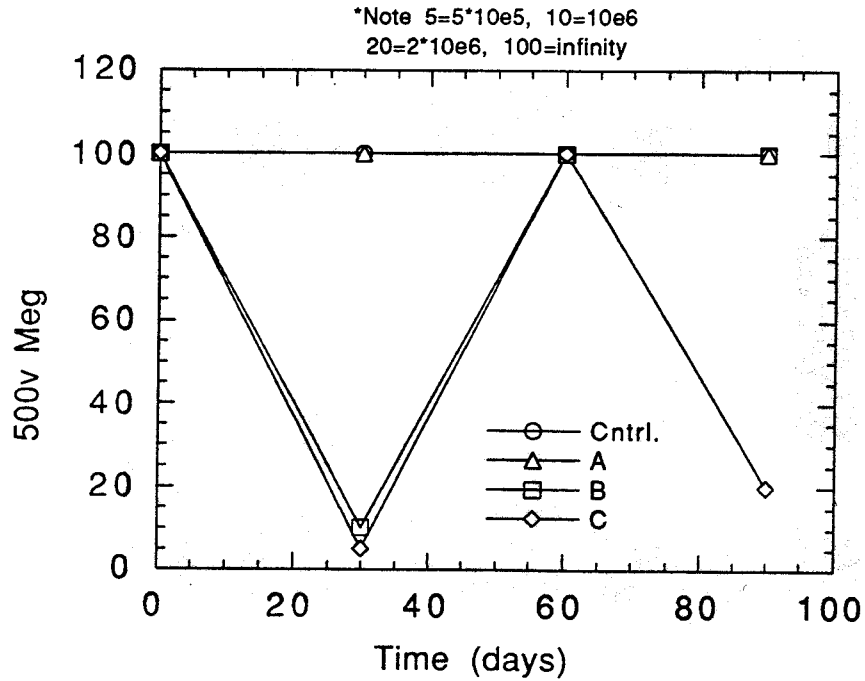Figure 4 Conductivity of Electrical boxes from Portable Shipboard Panel

Figure 5 Megger Measurements of Elecrical boxes from Portable Shipboard Panel