CORROSION INHIBITION OF ELECTRONIC METALS

USING VAPOR PHASE INHIBITORS

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ABSTRACT

Corrosion protection in electronics requires unique solutions. Complexity, miniaturization, airborne corrosives, "impressed" currents, etc. influence the occurrence of corrosion. Vapor phase inhibitors have been proven effective in applications analogous to those in electronics. We feel that these analogies are significant and vapor phase inhibitors should provide a degree of corrosion protection to all the metals found in electronic systems.

Three experimental procedures were used to test a large array of corrosive conditions. The first uses a high humidity environment with uncharged boards. The second utilizes high humidity with boards charged with 9V DC. And finally, the last experimental procedure exposes uncharged circuit boards to an environment polluted with H_2S .

Based on the test results the following conclusions were made:

- 1. Cyclic amine fatty acid salts and alcoholic amine salts enhance corrosion of metals used in the fabrication of electronic components.
- 2. Triazoles, cyclic amine nitrate salts and cyclic amine salts provided protection of selected metals used in the fabrication of electronic components.
- 3. The mixtures of vapor phase inhibitors tested provide protection of a cross section of metals used in the fabrication of electronic components under a wide variety of corrosive environments.

INTRODUCTION

Corrosion of complex electrical and electronic equipment is an increasingly serious problem, causing expensive and some times dangerous failures. The corrosion occurs during manufacturing, in shipping, storage and during field service. The following factors have influence on occurrence of corrosion:

- 1. Presence of moisture and corrosive agents: Cl^- , H_2S , SO_2 and other airborne corrosives.
- 2. Complexity and miniaturization of equipment causing design influenced galvanic effects, which seriously decrease service life of the equipment.
- 3. Increasing number of process control, or similar applications, for the electronics, causing their removal from air conditioned computer rooms into real industrial environments.
- 4. Presence of low voltage "impressed" currents, which accelerate dissolution of metals.

5. Contamination of critical surfaces during manufacturing and assembly adversely affecting adhesion and performance of conformal coatings, platings, etc.

Abbott (1) recognized that the critical levels of airborne corrdants have decreased several orders of magnitude, and it is now believed that the upper limit is around 10 parts per billion of total contaminants. This makes even air conditioned office environments potentially detrimental to sensitive circuitry. The most frequent forms of corrosion are general oxidation, localized corrosion or pitting, galvanic or dissimilar metal corrosion, crevice corrosion, ion migration, "whisker growth", etc.

Vapor phase inhibitors have been proven effective in applications analogous to those in electronics. Martin (2) found that vapor phase inhibitors were effective on only a few metals and corrosive to others making a dubious value to protection of complex metal systems. We feel that vapor phase inhibitors should provide a degree of corrosion protection to all the metals found in electronic systems. They perform by continuously depositing monomolecular layer, there is little possibility of changing even most sensitive surface properties, i.e. conductivity, resistivity, capacitance, etc. Vapor phase inhibitors have shown themselves to be an important factor in corrosion resistance, even in the aggressive environments of:

Marine and tropical climates, pulp and paper mills, steel mills and metal processing plants, fertilizer and food processing plants, power plants, power and gas transmission systems and telephone utilities.

The effectiveness of vapor phase inhibitors has been demonstrated in numerous field and laboratory tests. The following experiment performed by a major manufacturer of electrical/electronic enclosures is considered a classic example of their ability to provide protection (3). Four industrial relays with gold plated silver/cadmium oxide contacts were sealed in enclosures with the mechanism exposed and cycled over a million times. Contact electrical resistance checks were taken regularly in both normally open and closed contacts. All test enclosures were exposed to accelerated test conditions consisting of condensing humidity and increased temperature.

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Two unprotected enclosures showed increase in contact resistance in excess of 300,000 ohms after one million cycles. The relays in enclosures protected with a broad spectrum mixture of vapor phase inhibitors showed normal contact resistance, after completion of the corrosion test.

We used a general selection of metals used in the fabrication of electronic circuits and components to depict real world situations. Since the boards consisted of a large variety of metals a broad spectrum of vapor phase inhibitors were chosen. A survey of literature showed a lack of information dealing with corrosion in electronics. This paper will augment the information presently available in the literature and deal with the electrical/electronic applications of vapor phase inhibitors.

EXPERIMENTAL

Two separate tests were performed on the electronic circuit board assemblies, Figure 1. Electrical circuitry may be exposed to high humidity environments where the vapor phase inhibitor must protect against water vapor or an environment full of pollutants, i.e., Cl⁻, H₂S, SO₂; and high humidity. Therefore, the boards were sealed in self sealing polyethylene bags and exposed to high humidity conditions and high humidity H₂S conditions.

Throughout the entire experiment four steel zinc chromated machine screws were attached to the corners of the circuit boards. The reason for this is two fold:

1. To keep the polyethylene bags from making any contact with the boards thus providing a good continuous vapor phase environment.

2. Approximate a condition of hardware being fastened to a circuit board and to provide an area were a galvanic couple may exist.

The Condensing Humidity Test

Prepare 10% by wt. methanol solutions of the vapor phase inhibitors in Table 1. Sixteen 4.0 mil polyethylene self sealing bags were treated so 0.2 g of vapor phase inhibitor has coated the interior of each bag (two bags per vapor phase inhibitor). Sufficient time must pass to allow the methanol to evaporate and leave the vapor phase inhibitor residue.

Clean eighteen circuit boards by soaking in 1, 1, 2 trichloro 1, 2, 2 tri fluoroethane for two minutes to remove any fingerprints, flux, etc. Remove the boards and allow to reach equilibrium (25°C, 50% relative humidity) for five minutes before continuing.

Place a circuit board into each treated and marked bag, exhaust as much air as possible inside the bag and seal. The two remaining boards are sealed into untreated bags and used as the test controls.

The assemblies are placed into a two cycle condensing humidity chamber, (50°C 100% relative humidity; 23°C, 100% relative humidity) for a test duration of 30 days.

A parallel test is run using the above test procedure, with one difference. A 9V DC supply of electricity is applied to the circuitry of each board during the entire test.

The H₂S Test

The procedure in the Condensing Humidity Test is followed through the cleaning of circuit boards. Insert a circuit board into each treated and marked bag. A 50 ml beaker with 50 ml deionized water and 0.5 ppm $(NH_4)_2S$ is introduced into each bag. Exhaust as much air as possible and seal bag. The two remaining boards are handled as above and sealed in untreated bags and used as test controls.

The assemblies are set into a mechanical convection oven stabilized at 50°C for a test duration of three days.

RESULTS AND DISCUSSIONS

Actual electronic circuit boards were used throughout this investigation giving rise to some specific problems with the availability and type of metal substrate to be studied. Electronic circuit board components usually consist of a variety of metals and alloys, not to mention plastics and ceramics, so the ability to measure corrosion of "pure" substrates is nearly impossible. The boards that we used consisted of the normal potpourri of electrical components, i.e., resistors, electrolytic capacitors, transistors, I.C. chips, etc. lending many metal alloys available for testing. Refer to Table II for a breakdown of the specific parts that were evaluated and their multimetal alloy substrates available for testing. Along with a general selection of testable metals, a large spectrum of vapor phase inhibitors were chosen for our evaluation.

Several chemical structure categories of vapor phase inhibitors are represented in our study. General chemical names have been assigned to the actual inhibitors tested so not to reveal any proprietary chemicals and so any conclusions and recommendations can be done categorically. A list of the vapor phase inhibitors studied is given in Table I, which includes two mixtures of vapor phase inhibitors to determine whether synergistic protection properties are afforded by each compound within the mixture.

To accurately qualify the type of corrosion found and quantify the amounts, optical microscopy was chosen as the test method for corrosion evaluation. Many useful parameters have been examined using this method:

- 1. Type of corrosion attack.
- 2. Amount of surface area corroded.
- 3. Effects of corrosion or inhibitor on the circuit board itself.

With these results an accurate and comprehensive determination of vapor phase inhibition is possible.

To further qualify the test results, the diffusion rate of water vapor through polyethylene bags has been calculated. Self sealing polyethylene bags (8"x8") were used to enclose the test circuit boards. Only the enclosures that were tested using The Condensing Humidity Test are affected by the water vapor diffusion rate since the source of water vapor is external to the enclosures and must pass through the bags to the inner environment and create a high humidity atmosphere. The value obtained for water vapor transmission through a low density polyethylene bag is (4):

1.4 g/100 in²/24 hour/mil

A more meaningful transmission rate is obtained when the area of the enclosure surface (128 in²) and the thickness of the polyethylene (4.0 mil) is applied to this value. The following rate is calculated:

0.4 g/24 hour

When this rate is plotted as grams of water vapor transmitted vs. time, Figure 2 is the result. This graph shows a linear accumulation of water vapor over the test duration thus allowing a gradual increase of corrosivity and simulating some rather severe real world situations.

The Condensing Humidity Test

A summary of test result is found in Table III. It can be seen that the diode and jumpers were not reactive in this test. However, an increase of corrosion on the diode is indicated with the alcoholic amine carboxylate as well as an increase of corrosion on the jumpers with cyclic amine carboxylated fatty acid (C_{16}). The bolts showed conclusive results as to levels of protection and corrosion, with attack evident from both cyclic amine carboxylated fatty acids. Excellent protection of the bolts with the cyclic amine carboxylated and mixture of cyclic amine carboxylate/alcoholic amine carboxylated have been observed. Alcoholic amine carboxylate and cyclic amine carboxylated nitrate show an ability to protect the capacitors while the triazole and mixture of triazole/cyclic amine carboxylated nitrate/cyclic amine carboxylate protected solder. Most of the corroded surfaces exhibited general pitting along the component leads. Low level galvanic corrosion was observed where bolt/solder couples were made. An overview of the test results indicated that overall inhibition was afforded by both vapor phase inhibitor mixtures and triazole.

The Condensing Humidity Test CHARGED

Refer to Table IV for test results. The jumpers were found to be less reactive than the other components with the exception of cyclic amine carboxylated fatty acid (C_{16}) which attacked the jumpers. The alcoholic amine carboxylate attacked solder to a high degree while triazole and the mixture of triazole cyclic amine carboxylated nitrate/cyclic amine carboxylate protected solder. Inhibition of the capacitor was afforded by the triazole. Cyclic amine carboxylated fatty acid (C_{16}) provided significant protection of diodes with only traces of corrosion on their leads.

"Whisker Growth" was produced on solder as a result of the alcoholic amine carboxylate and the cyclic amine carboxylated fatty acid (C_{18}). Galvanic corrosion of the bolt/solder joints behaved according to the results tabulated in the bolt section of Table IV. The results indicate that triazole performed best overall with cyclic amine carboxylate providing excellent cross sectional protection against corrosion.

The H₂S Test

The large percentage of corrosion on test controls in Table V indicate that out of all tests performed, the H_2S Test was the most corrosive. The results also demonstrate that the cyclic amine carboxylated fatty acids enhance corrosion on the bolts, capacitors and solder and are not effective on diodes or jumpers. Triazole performed better than other vapor phase inhibitors tested on solder as did cyclic amine carboxylate on capacitors.

Black corrosion (tarnish) was found to be the characteristic form of corrosion on the diodes while "whisker growth" dominated the class of corrosion exhibited on solder, especially the solder tested with alcoholic amine carboxylate. The mixture of cyclic amine carboxylate/alcoholic amine carboxylate and cyclic amine carboxylate exhibited good protection on the substrates tested.

CONCLUSION

The point of this paper was to survey classes of vapor phase inhibitors and to test their effectiveness as vapor phase inhibitors on electronic metals. Selection of vapor phase inhibitors for electronic applications should be done with great care taking into consideration the results and conclusions of this study.

From Tables III, IV, V and the results provided the following conclusions can be made:

- 1. Cyclic amine carboxylated fatty acids attack bolts, solder and jumpers.
- 2. Alcoholic amine carboxylate will enhance corrosion of diodes.
- 3. Triazoles provide corrosion protection on bolts and solder.
- 4. Cyclic amine carboxylated nitrate protects components on uncharged circuit boards under high humidity conditions.
- 5. Cyclic amine carboxylate protects circuit board components exposed to polluted high humidity environments.
- 6. The mixtures of vapor phase inhibitors tested provided corrosion protection of general metals used in the fabrication of electrical/electronic components under a wide variety of corrosive environments.