

VOLATILE CORROSION INHIBITORS
FOR PROTECTION OF ELECTRONICS

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ABSTRACT

As electronic components become increasingly complex, the degree of corrosion that can be tolerated is greatly decreasing. A method of protecting electronic components from corrosion should not alter performance of circuitry or contacts, and should offer some degree of protection to a wide variety of metal alloys. Steps taken to reduce corrosion of electronic components to date have only been partially successful, therefore, new methods need to be adopted to further reduce corrosion of electronic components.

The scope of this paper is to show that a properly formulated mixture of volatile corrosion inhibitors can be used to effectively protect electronic metals from corrosion. Comparisons of three volatile corrosion inhibitors were carried out on a variety of metal test specimens in corrosive environments.

INTRODUCTION

Electronic components are a complex assembly of metallic and non-metallic materials. Corrosion of the metallic components can readily occur in the presence of moisture with the process being assisted or accelerated by corrosive contaminants often present at micro-contamination levels. Sources of contamination that play an important role in the corrosion of electronic materials are often derived from a wide variety of atmospheric pollutants, low levels of contaminants present in packaging materials, and as a result of human handling.¹

Given their complexity, there are many mechanisms by which corrosion of electronic components can occur. These include pore and creep corrosion of base metals plated with a noble metal, corrosion caused by deposited pollutants in combination with moisture, fretting corrosion, localized and stress corrosion in the presence of corrosive contaminants (i.e. chlorides), galvanic corrosion resulting from contact of dissimilar metals, and electrolytic corrosion resulting from applied potentials normally found in electronic devices. Steps taken to eliminate corrosion problems including hermetic sealing of components in cavities, use of protective coatings, encapsulation, use of noble metal platings, increased use of more corrosion resistant metal alloys, and the use of moisture absorbing dessiccants have all served to reduce, but not eliminate corrosion in electronic components.²

Volatile Corrosion Inhibitors (VCIs) can provide an effective means of protecting electronic components from corrosion. These compounds have sufficient vapor pressures (10^{-3} to 10^{-5} mmHg at 70° F) to allow vaporization and subsequent condensation and adsorption on metal surfaces as a mono-molecular passivating layer. The ultra-thin protective layer does not interfere with conductivity or resistivity of the base metal. This direct method of corrosion protection by means of metal passivation in many cases is superior to traditional indirect methods of corrosion protection such as the use of drying agents and protective coatings. We feel that in many applications the use of these types of inhibitors coupled with steps that industry has taken to reduce corrosion of electronic assemblies will further reduce this industry wide problem.

The specific objectives of the study undertaken for this paper are:

1. To determine the positive or negative effects of several volatile corrosion inhibitors on metals commonly used in electronics applications.
2. To determine the extent of protection provided by several corrosion inhibitor compounds on various metals in the presence of moisture and corrosive contaminants such as hydrogen chloride and volatile sulfide compounds.
3. To briefly review expected inhibitor mechanisms to provide a better understanding of inhibitor/metal interactions.

The volatile corrosion inhibitors to be studied are DICHAN (dicyclohexylammonium nitrite), tolyltriazole and a proprietary mixed amine salt compound. DICHAN is probably the first compound whose protective properties in the vapor phase has been noted. This material has been used extensively for the protection of mostly ferrous based metals. Tolyltriazole has been widely used in protecting copper alloys as a surface treatment and in the vapor phase. Tolyltriazole has probably had the most widely accepted use as an inhibitor in the electronics industry to date. Another group of inhibitors based on salts of aliphatic amines or alcoholumines and carboxylic acids are also gaining favor as multi-metal inhibitors. Mixtures of different amine salts to optimize vapor pressures of the mixture and inhibitive properties toward a wider variety of metals appears to offer potential as an inhibitor for multi-metal electronic systems.

EXPERIMENTAL

To minimize the myriad of complexities associated with the corrosion of electronic components, an actual electronic device was not used in these experiments, rather test specimens of individual metal alloys commonly used in electronics were evaluated by exposing the metal to the inhibitor vapors in a corrosive environment. The corrosive environments chosen for these experiments included high humidity exposure, high humidity with hydrogen chloride added as a corrosive agent, and high humidity with a volatile sulfide compound added as a corrosive agent.

The test apparatus was set up as follows:

1. 500 milligrams of the volatile corrosion inhibitors were sprinkled on the bottom of a 1000 ml capacity glass jar.
2. A beaker containing 50 ml of deionized water was placed in each jar. In the cases where corrosive agents were used, the deionized water contained 50 ppm hydrogen chloride or 1 ppm ammonium sulfide.
3. The cleaned and prepared metal test specimens were placed into the jars containing the corrosive media.
4. The jars were sealed with a screw top lid. The junction of the lid and jar was then sealed with a low moisture vapor transmission rate tape.
5. The test jars were allowed to set at ambient conditions for 16 hours. The jars were then placed in an oven operating in a cycle of 50°C for 12 hours followed by a shut-off period of 12 hours in order to create a condensing humidity type of environment.
6. After 30 days of continuous cycling in the oven, the specimens were removed and examined for the degree of oxidation or tarnish observed. Each specimen was

evaluated according to the rating system outlined in Table 1 relative to a control specimen.

RESULTS AND DISCUSSION

Corrosion Inhibitor Rating System

Table I outlines the categorization system used to determine the degree of oxidation and/or tarnish present on each test specimen.

The rating system shows whether the VCI compound exhibited positive, negative or neutral effects on the test specimen compared to a control with no VCI compound present. It also shows which inhibitor performed best on each metal test specimen.

Corrosion in a High Humidity Environment

Table II lists the results obtained with metal test specimens exposed to VCI compounds in a condensing humidity environment.

In this case, DICCHAN appeared to accelerate corrosion of tin based solder, copper, brass, and cadmium alloys tested. Favorable results were obtained on aluminum and steel. No significant effects were noted on lead based solder and nickel alloys.

On cadmium, tolyltriazole appeared to offer a marginal degree of protection, whereas the mixed amine salt compound appeared to have accelerated corrosion. Conversely, the mixed amine salts provided excellent protection to low carbon steel whereas tolyltriazole offered marginal protection.

Corrosion in a Hydrogen Chloride Contaminated Environment

Table III lists the results obtained with metal test specimens exposed to VCI compounds in a condensing humidity environment with hydrogen chloride added as a corrodent.

The results obtained appear to roughly correlate to those obtained in a high humidity environment listed in Table II. The added hydrogen chloride in this test does not appear to have significantly increased the extent of corrosion observed on the metal test specimens.

Corrosion in a Sulfide Contaminated Environment

Table IV lists the results obtained with metal test specimens exposed to VCI compounds in a condensing humidity environment with a volatile sulfide added as a corrodent.

The control specimens of copper and brass showed particularly severe oxidation/tarnish compared to the other exposure environments. This was expected since the oxidation/tarnish of copper and brass alloys are particularly sensitive to sulfide compounds.

Table IV also shows the excellent results obtained on copper and brass with tolyltriazole and the mixed amine salt compounds. Again, DICHAN appeared to accelerate the attack on these materials.

The results on other metals tested appears to be similar to the results outlined for the high humidity environment (Table II).

Initially, the volatile sulfide corrodent was added to water at a level of 5ppm. However, it was found that this level of corrodent was too severe for any of the VCI compounds to overcome on copper and brass alloys. It was found that a more realistic concentration of the volatile sulfide compound was at 1 ppm in water.

Volatle Corrosion Inhibitor Mechanism

The mechanism of protection provided by volatile corrosion inhibitors has been studied mostly on ferrous based metals. It is not precisely known what the exact mechanism of protection is, but is believed that the monomolecular inhibitor coating that condenses from the vapor phase on ferrous metal surfaces is dissolved by moisture to create the ions necessary for protection. The weakly adsorbed inhibitor ions passivate the surface by saturating the metal gas interface and by polarization of the metal.^{3,4}

The passivation mechanism on non-ferrous metals has not been as extensively studied. Tolyltriazole is believed to interact with the cuprous oxide film normally present on copper surfaces, forming a protective polymeric triazole film.⁵ It has been further suggested that certain amine salt vapors also interact with cuprous oxides to form organometallic compounds which may play an important part in the overall protective mechanism.⁶

Table V lists results obtained by first exposing carbon steel and copper panels to the mixed amine salt and tolyltriazole compounds as outlined in the experimental procedure. After the exposure period the panels were suspended in a condensing humidity cabinet. The results indicate that there was no further oxidation of the copper panels, but the carbon steel panels showed uniform general corrosion over the entire metal surface.

OBSERVATIONS/CONCLUSIONS

1. The volatile corrosion inhibitor DICHAN is not an effective inhibitor for electronics because of its adverse effects toward several common metals used in electronic applications.
2. The volatile corrosion inhibitors tolyltriazole and the mixed amine salt compounds appear to be effective inhibitors for electronic applications because of the favorable effect observed on a wide variety of metals. However, neither of the inhibitors can be considered as universal for all metals.

3. The mechanism of inhibitor passivation of metal surfaces appears to be related to the character of the metal substrate. Test results seem to indicate that tolyltriazole and the mixed amine salt compounds offer a lasting protection to copper surfaces even after the bulk inhibitor compounds are removed. On the other hand, the inhibitors do not offer lasting protection to carbon steel once the bulk of the inhibitor has been removed. Weak adsorption of inhibitor ions may require continual replenishing on the metal surface from the bulk inhibitor.

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