VOLATILE CORROSION INHIBITORS
FOR ELECTRONIC MATERIALS

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Techniques for improving corrosion resistance of electronic
materials are described. The surfaces of various metals are
treated with volatile corrosion inhibitors (VCIs) containing
triazoles, amines, carboxylic acids and/or their salts and esters.
Accelerated corrosion tests are performed at elevated temperature
and humidity. VCIs have been found to provide good protection
for a variety of metals.

INTRODUCTION

Corrosion protection of electronic equipment and components has become more difficult because of the complexity and miniaturization of components, the presence of airborne contaminants and the microcontamination from processing and assembly operations. Volatile corrosion inhibitors (VCIs) provide a simple and effective means of protecting electronic components from corrosion. These compounds have low but significant vapor pressures (e.g. 10^{-3} to 10^{-5} mm Hg at 70°F) to allow vaporization and subsequent adsorption on mental surfaces as a thin layer. The adsorption is often physical except a few chemisorption cases such as triazoles on copper. This thin layer, unlike thick organic coatings, does not alter the electrical resistance of metals. Being in the vapor phase, VCIs can easily access hard-to-reach areas commonly found in electronic components. Its low vapor pressure allows corrosion protection for a long period, up to 24 months.

The method of applying VCIs includes: a) dipping or spraying electronic components with VCI solution, (b) impregnating foams with VCI solutions which are placed with operating components in an enclosed space, e.g. VCI devices, emitters, and tapes, and c) impregnating or coating papers and extruding or coating polyethylene films with VCI solutions which are used as packaging materials. In this study, the first method is used for applying VCIs.

The protection mechanism of VCIs is not completely understood. Numerous formulations of VCIs are described in a review paper of Singh and Banerjee (1) for ferrous and non-ferrous metals. Formulations for corrosion protection of copper, aluminum and silver with impregnated papers are discussed by Heidemann (2). Singh, Sabita and Altekar (3) reviewed a number of formulations of corrosion inhibitors for silver.

The amount of inhibitors needed to protect metal in a given volume is usually determined empirically. For VCIs to be effective, the inhibitors must diffuse to and become adsorbed on the metal surface in a relatively short time, typically 48 hours. In a recent paper of Polteva and Persiantseva (4), the time required for VCIs to reach a metal surface has been calculated by solving Fick's second law of diffusion in one dimension. To predict the efficiency of VCIs, Agres and Altsybeeva (5) have derived a relation which shows that the efficiency of an inhibitor increases with an increase of its saturation pressure and diffusion coefficient and decreases with the minimum protective concentration. It is also important to follow the degree of protection of metals without opening the enclosure. Rozenfel'd, Samoilenko and Mudzhiri (6) determined the effectiveness of VCIs by measuring the change of ohmic resistance of unprotected (control) and protected copper and iron specimens packaged in polyethylene films.

In addition to the use of corrosion inhibitors, another approach is to remove sulfur-containing gases from the environment for preventing silver tarnishing. Papers treated with compounds which absorb and react with hydrogen surfide are placed in an enclosed space (1-3).

In this paper, techniques for improving corrosion resistance of electronic materials are described. The surfaces of various metals are treated with VCIs containing

triazoles (R_1), amines (R_1-N-R_3),

carboxylic acids (RCOOH) and/or their salts and esters. Triazoles are known for their ability of protecting copper and silver. Amines and amine salts are for the protection of aluminum and ferrous metals. Carboxylic acids are for the protection of ferrous metals.

EXPERIMENTAL

In this work, corrosion inhibitors for electronic materials are formulated by dissolving several compounds in a solvent. A proprietary formula, designated in this paper as Formula A and consisting of a mixture of a carboxylic acid, a triazole and a amine, is used in this study. Some requirements are essential for the solvent used in dissolving corrosion inhibitors. It has to be non-conducting a and non-toxic, evaporate rapidly, form dry films, and wet the surfaces of electronic materials. Chlorofluorocarbon (CFC)-113 (CCl_2F-$CClF_2$) is used as the solvent. The search for a new solvent is necessary because of the ozone-depletion potential of the CFC's. A quick substitute of l,l,l,-trichloroethane is used in a new formula, designated here as Formula B, which also combines compounds of a carboxylic acid, a triazole, and an amine. Candidates substitutes for CFC-113 include hydrochlorofluorocarbon (HCFC)-141b (CH_3CCl_2F) and HCFC-123 ($C_2HF_3Cl_2$); however, these are not available commercially. Another candidate substitute is N-methyl pyrrolidone

(NMP,   ). This has been used to clean circuit boards and it is compatible with

polyethylene or polypropylene-encapsulated components. Once applied, NMP does not evaporate readily but a dry film is obtained within two days. Its non-flammable property makes it a good option for application to live circuits. A formula containing a mixture of a triazole, a carboxylic acid and an amine in NMP is designated here as Formula C. Because of the high surface tension of this solvent, there is a problem of creeping on copper panels dip-coated with this formula. When a surfactant is incorporated in a variation of this formula, good wetting ability is obtained.

Accelerated corrosion tests are performed at elevated temperature and humidity. The extent of protection provided by VCIs on metals is determined. Test panels of 1.5 x 3" x 1/16" are cleaned with methanol before use. For each metal, one panel is untreated, another one is sprayed with Formula A, and another one is dipped in an ASTM D-1748 humidity cabinet with a relative humidity of 100% and temperature of $50^{o}C$.

RESULTS AND DISCUSSION

The number of days to failure of the metal panel when exposed in the humidity cabinet is summarized below and shown in Figure 1 for each of the VCI formulations and metals.

	Ag	Solder	Cu	Brass	Al	Steel	Galva. Steel	Alumi. Steel	Cast Iron
Control	3	10	4	1	1	3	1	1	complete
Formula A	18	66	>80	>80	1	16	4	4	complete
Formula B	15	>80	11	>80	15	63	6	8	near complete

Both untreated cast iron and cast iron treated with Formula A were completely covered with rust within one day. Cast iron treated with Formula B showed brown spots near edges after one day. While Formula B provided very good protection for aluminum, steel and cast iron, Formula A protected copper better than Formula B. Both were very effective in protecting solder and brass.

From these results, it is desirable to combine the copper protection property of Formula A and the aluminum protection property of Formula B in a new formula. Corrosion tests for this new formula including humidity test and flowing mixed gas test are conducted. The latter test was developed by Abbott (7-10). A class II environment is employed with pollutant concentrations of H_2S-10 ppb, Cl_2-10 ppb, NO_2-200 ppb, 70% relative humidity, and a temperature of $30^{o}C$. Test panels of various metals are checked twice on the first day and once a day on the following days. In addition to visual inspection of corrosion signs, contact resistance of test panels is measured. Test results will be available shortly.

Corrosion inhibiting properties of mixtures of different VCIs have been examined. VCIs have been found to provide good protection for a variety of metals.

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FIGURES

Figure 1. ASTM D-1748 Humidity Cabinet