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## Aging, Stressing and Solderability of Electroplated and Electroless Copper

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**Aging, Stressing and Solderability of  
Electroplated and Electroless Copper**

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Abstract

Organic inhibitors can be used to prevent corrosion of metals have application in the electronics industry as solderability preservatives. We have developed a model to describe the action of two inhibitors (benzotriazole and imidazole) during the environmental aging and soldering process. The inhibitors bond with the metal surface and form a barrier that prevents or retards oxidation. At soldering temperatures, the metal-organic complex breaks down leaving an oxide-free metal surface that allows excellent wetting by the molten solder. The presence of the inhibitor retards the wetting rate relative to clean copper, but provides a vast improvement relative to oxidized copper.



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## Introduction

Organic solderability preservative (OSP) coatings are receiving renewed interest by the electronics and computer industries in response to productivity demands placed on new surface finishes for solder processing. Pre-tinned solder coatings have been the industry standard. With a variety of environmental (CFC and Pb elimination), design (co-planarity), and metallurgical (solder thickness and intermetallic dewetting) issues facing printed wiring board (PWB) manufacturers, future solderable conductive features (lands, vias, etc.) will differ from the current solder coated finishes. One promising approach is bare copper coated with a protective organic inhibitor.

OSP coatings are not new to the electronics industry [Ref. 1-8]. Solder wettability can be maintained for extended periods of storage with these OSP's. They have been used primarily to inhibit chemical reactions between the ambient environment and conductive metallic surfaces on a PWB. The coatings slightly reduce solder wettability during initial contact with molten solder (lower wetting rates and longer times), but they typically satisfy the wetting criteria required in standard soldering specifications.

There are two general classes of OSP's. The first is based on an azole chemistry and is commonly referred to as an inhibitor. Imidazole, benzotriazole, benzimidazole, and tolyltriazole are typical azole OSP coatings. They generally form thin films that chemically bond with metal surfaces. The second class of OSP is rosin-based and commonly referred to as a prefluxer. Preflux coatings adhere to the metal substrate, but do not chemically bond to it. They are generally much thicker and tackier than the azole coatings.

With the international push towards more environmentally compatible manufacturing technologies, the OSP coating of bare copper PWBs is getting more attention. Several industrial and academic studies have been initiated with the goal of identifying acceptable processing conditions for applying OSP's to PWB assembly. The NCMS PWB Surface Finishes Team and Sandia National Laboratories' Center for Solder Science and Technology have been characterizing several OSP coatings on bare copper surfaces. These efforts are aimed at the determination of the effects of simulated aging and flux type on the solder wettability of inhibited Cu samples.

This paper reports results for electroplated and electroless Cu inhibited by imidazole(IMD) and benzotriazole (BTA). Corrosion data from aging tests and wetting balance data on inhibited and bare copper are reported.

## Materials and Sample Preparation

Samples of both electroless (EL) and electroplated (EP) Cu were obtained from AT&T. Material was supplied as plated panels. All material was coated with imidazole during processing at AT&T. Individual test coupons (nominally 25 x 25 mm) were cut from the panels for solderability testing. Similar samples were initially used for corrosion studies. However, due to absorption of materials from the flowing gas, weight changes were unreliable and these samples were not used for corrosion testing. Samples were degreased with trichlorethylene and isopropyl alcohol. For the corrosion studies, copper was sputter deposited on AT cut quartz crystals for use in a quartz crystal microbalance. To apply BTA to the copper panels, the imidazole was first removed by etching in 10% HCl solution for 3 minutes at room temperature. The samples were then rinsed in D.I. water followed by application of BTA.

The BTA solution consisted of 98% BTA dissolved in isopropyl alcohol to a concentration of 0.033 molar. The BTA coatings were applied to the copper coupons immediately after etching. The coupons were dipped in the inhibitor solutions for one minute. A deionized water rinse, isopropyl alcohol rinse, and final drying with flowing nitrogen gas followed the BTA application.

Wetting balance test samples were supplied by AT&T, already coated with imidazole (IMD). When required, IMD was applied by dipping in an alcohol-based solution of IMD that was prepared following the BTA procedure.

All samples were fluxed and allowed to dry approximately ten minutes prior to wetting balance testing. Similar procedures were used on samples set aside for the aging experiments. Aged coupons were solder tested immediately following their removal from the environment.

## Experimental

Accelerated aging was performed in our Facility for Atmospheric Corrosion Testing (FACT)[5], a flowing mixed gas chamber. Conditions in the chamber are designed to simulate exposure to standard industrial environments [9]. For this study a class II environment was chosen which represents an indoor industrial environment and contains 10 ppb H<sub>2</sub>S, 200 ppb, NO<sub>2</sub>, and 10 ppb Cl<sub>2</sub> at 35°C and 70% relative humidity. Samples were exposed to this environment for 24 hours, which simulates eight months of industrial shelf storage.

Solder wettability was measured with a commercial wetting balance. The test method gives quantitative information on the wetting behavior of solder on the metal substrate under a specific set of

conditions. Wetting force versus time data provide a quantitative means to compare different materials and test conditions. The wetting balance tests were performed with 60Sn-40Pb (wt. %) solder at 245°C. The immersion times were 10 seconds. The balance tests used an immersion rate of 20 mm/s and an immersion depth of 1 mm. Five tests were typically conducted for each surface condition. A rosin, mildly activated (RMA) flux was used throughout the initial study.

## Results & Discussion

Samples of both the electroless and electrodeposited Cu were examined with a scanning electron microscope (SEM) to determine relative differences in surface morphology. Figure 1 shows SEM micrographs of the two surfaces. The electroless surface exhibits more macroscopic features as seen in the low magnification micrograph. A fairly coarse nodular surface is visible. The EP Cu, on the other hand, appears to be smoother on a macroscopic level, with no evidence of the large surface irregularities seen with the EL Cu. However, neither surface is smooth, as seen in the high magnification SEM photographs. The EL Cu surface tends to be more rounded, with features that appear like pits on the surface. The EP Cu surface exhibits very angular features that appear as ridges or plates. The corners are much sharper and more pointed. Due to this surface roughness, both surfaces would be expected to have surface areas considerably larger than the macroscopic area.

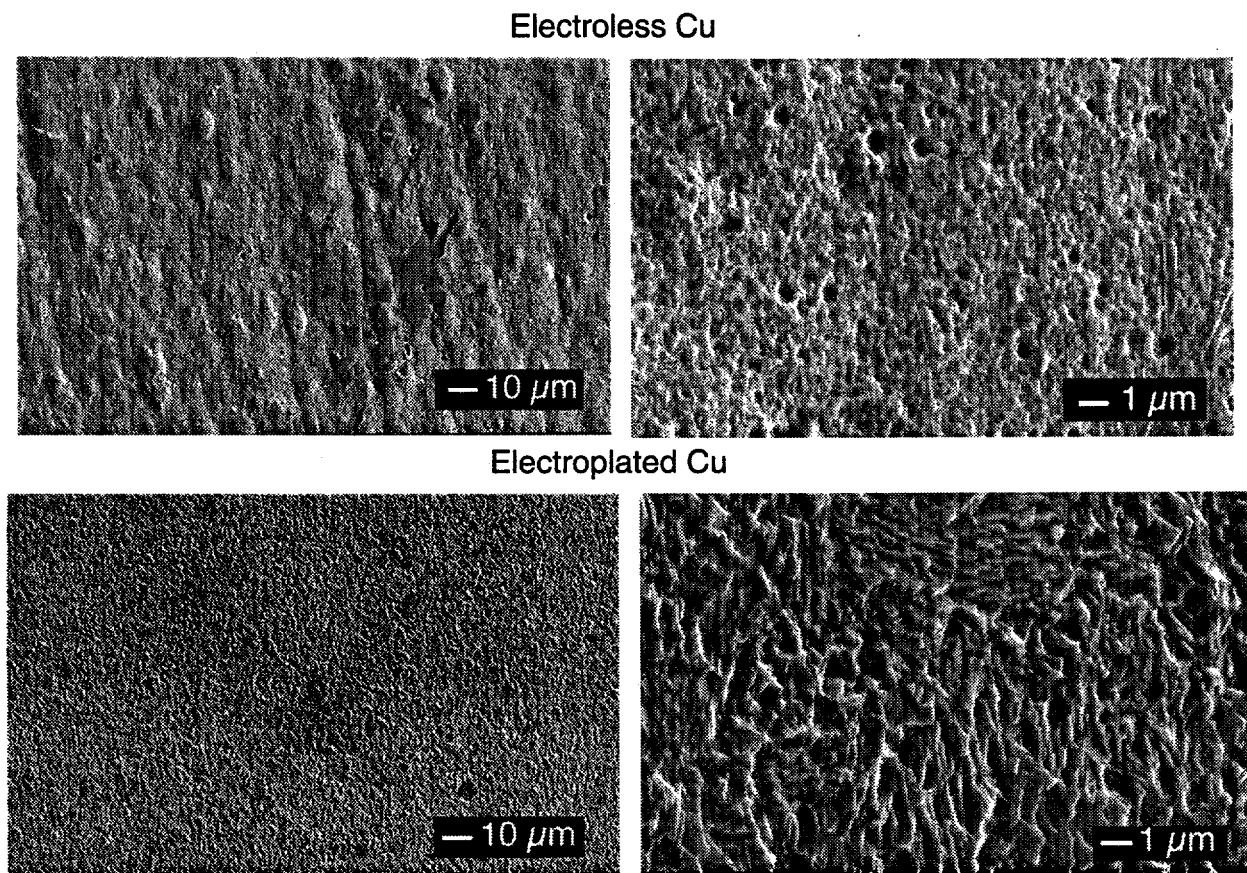


Figure 1. SEM micrographs of electroless and electroplated Cu surfaces. Both surfaces exhibit similar characteristics, but the electroplated surface features are sharper and more angular.

Figure 2 shows the corrosion behavior of sputter deposited Cu subjected to a Class II environment. Both the inhibited and uninhibited samples exhibit similar behavior. There is an initial sharp increase in mass (probably due to adsorption of water vapor and/or gas species on the surface) followed by approximately linear corrosion kinetics. Both the BTA and IMD exhibit identical kinetics with a sulfidation rate of 0.016  $\mu\text{g/hr}$ . The uninhibited Cu exhibits a substantially higher corrosion rate of 0.04  $\mu\text{g/hr}$  or about 2.5 times the rate for the inhibited Cu.

### Atmospheric corrosion of Cu

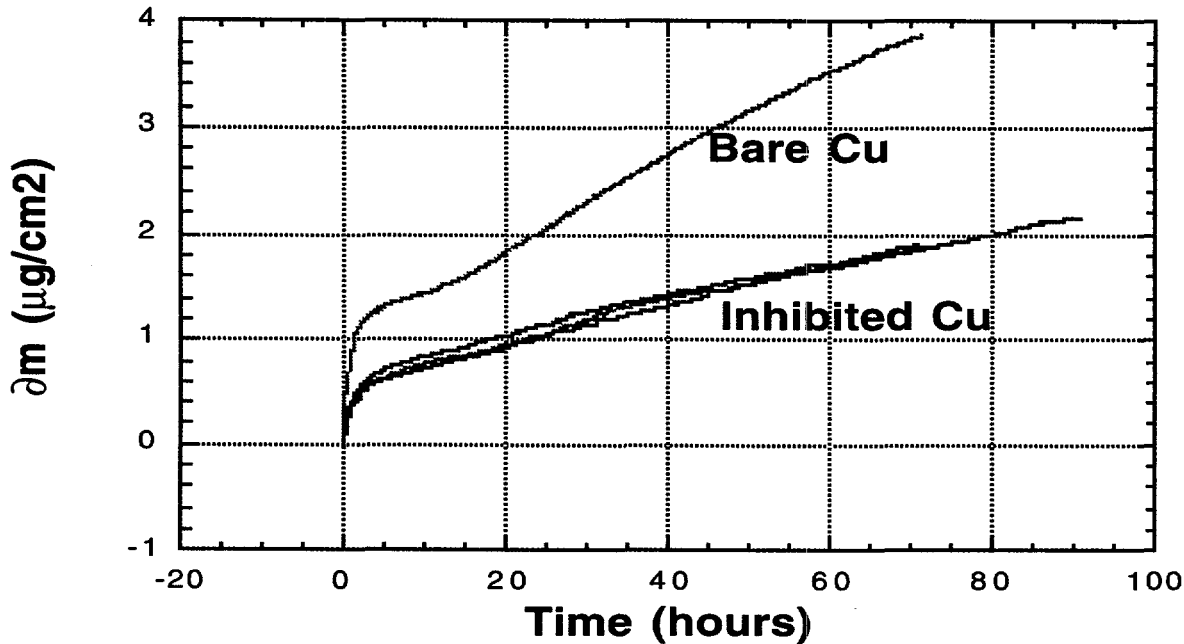


Figure 2. Atmospheric corrosion of Cu exposed to Class II environment.

Figure 3 shows the wetting behavior for electroless (EL) and electroplated (EP) Cu and shows the effect of the degreasing process on solderability. Based on these curves, the degreasing process has no detrimental effect on the wetting process. In Figure 3b (EP Cu), there appears to be two distinct slopes or wetting rates observed. There is a break in the curve (indicated by the arrow) before the wetting force has reached a maximum value, where the wetting rate slows down. This feature is absent in the curves for EL Cu (Fig 3a).

Figure 4 gives a comparison between etched EP and EL Cu. Both sets of samples were etched to remove the imidazole prior to testing. No difference is seen between these sets of data, indicating no difference between EP and EL Cu. However, it is possible that the etching process removed some copper in addition to the inhibitor, thus modifying the surface. If this is the case, the above comparison may not be valid. Note also, that there is no plateau in the wetting curve for the EP Cu samples. This indicates that the change in slope shown in Figure 3b is a result of the imidazole on the surface.

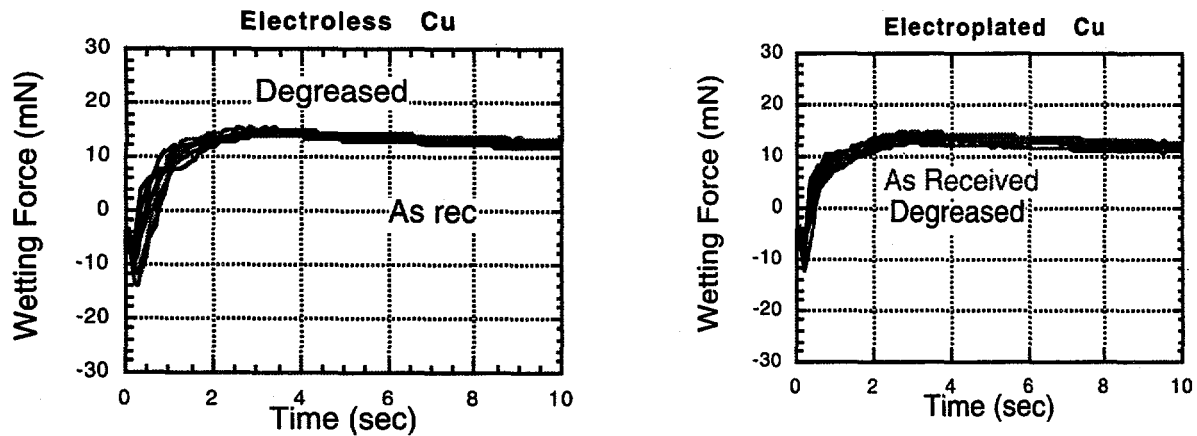


Figure 3. Wetting balance results for EP and EL Cu showing the effect of the degreasing process.

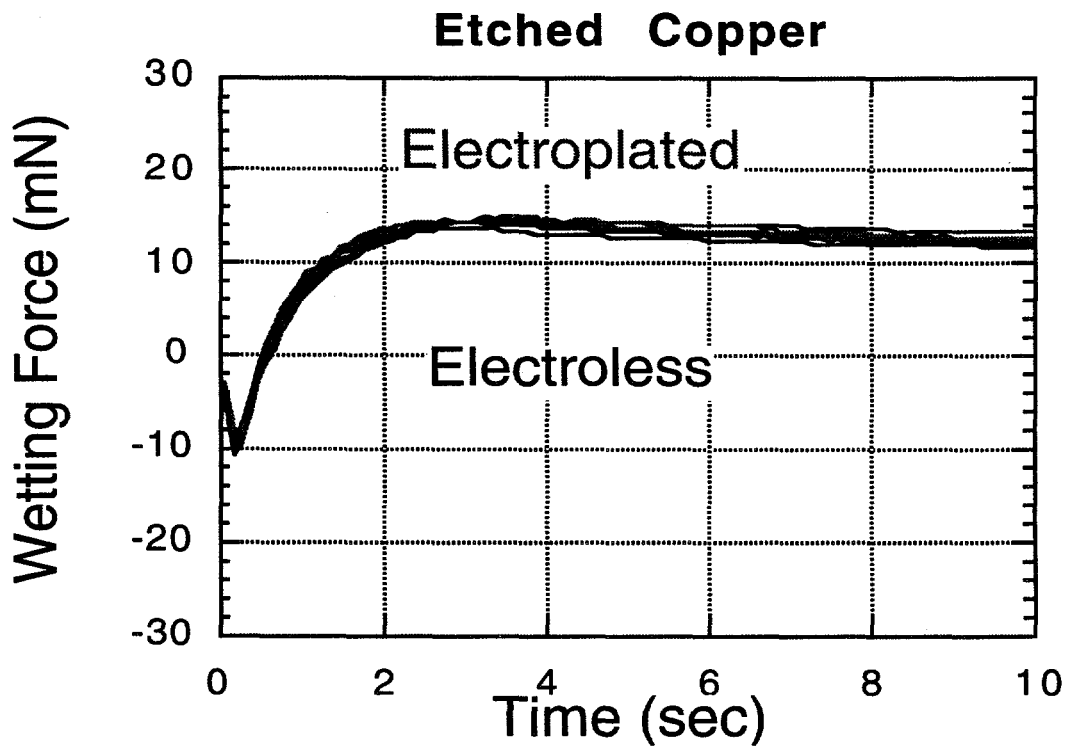


Figure 4. Wetting balance behavior of EP vs EL Cu. Samples were etched prior to testing to remove imidazole..

Copper reacts readily with atmospheric contaminants ( $H_2S$ ) resulting in a loss in solderability. Figure 5 presents data for both electroless and electroplated Cu exposed for 24 hours in a Class II environment (equivalent to 8 months of shelf storage). Exposure to a Class II environment results in the formation of a corrosion product film (predominately copper sulfide) which impedes the soldering process. Note the extremely slow wetting rate for the exposed copper. Even after 10 seconds, the samples do not show appreciable wetting. This indicates that the atmospheric corrosion process can significantly degrade the soldering operation.

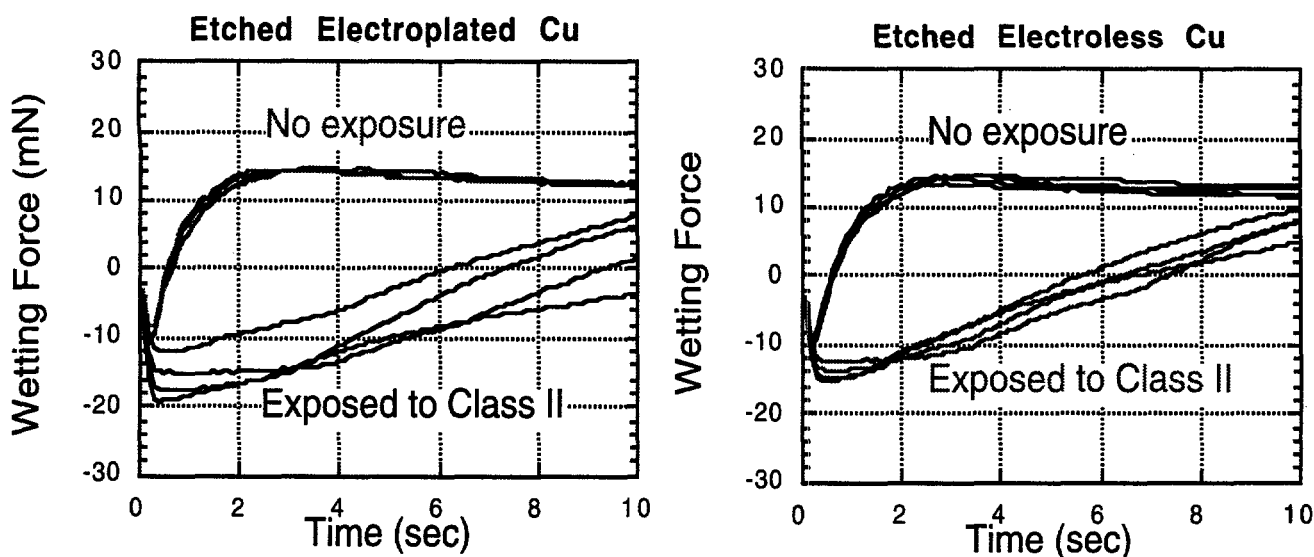


Figure 5. Effect of class II exposure on wetting balance behavior of Cu.

Organic inhibitors can be used to prevent or retard the corrosion process. In this study, imidazole and benzotriazole were investigated. The inhibitor is an organic molecule that reacts with the surface atoms to form an inhibitor-metal compound, which acts as a protective film to prevent or limit corrosion. During the soldering process, the inhibitor must be removed to allow the solder to wet the metal surface. Data show that the inhibitor, being thermally unstable at soldering temperatures, is removed from the surface during the soldering operation. Figure 6 presents the results of solderability tests of imidazole and benzotriazole inhibited copper. Both inhibitors slow the wetting process relative to clean copper, with the BTA producing a more pronounced effect. With both inhibitors, the maximum wetting force is comparable, indicating that both inhibitors are removed during soldering. However, it appears that the BTA bonds more tightly, or forms a thicker film than does the IMD, making it more difficult to remove. This results in a slower wetting rate, longer time to 90° turn-around, and a longer soldering time. However, the time is not prohibitive relative to most soldering processes.

While it is important for solder to wet inhibited copper, the real test of the inhibitor's utility is seen following atmospheric exposure. Bare Cu, exposed to the atmosphere, can lose solderability with time. As shown in Figure 5, the same is true for copper exposed to a Class II accelerated environment. Figure 7 shows the wetting balance behavior for inhibited copper exposed to the FACT Class II environment. Three observations are immediately evident. First, wettability of the imidazole sample seems to degrade with FACT exposure. Second, exposure does not affect the behavior of the BTA inhibited Cu. Third, both inhibitors provide acceptable solderability relative to a production environment. Again, a plateau region or a change in the slope of wetting balance curve was observed for the imidazole inhibited samples. The cause of this slope change is unknown. Note also, that there is more scatter in the data following FACT exposure. This is to be expected, since the inhibitor does not completely prevent oxidation/sulfidation of the Cu, but only limits the degree of the reaction.

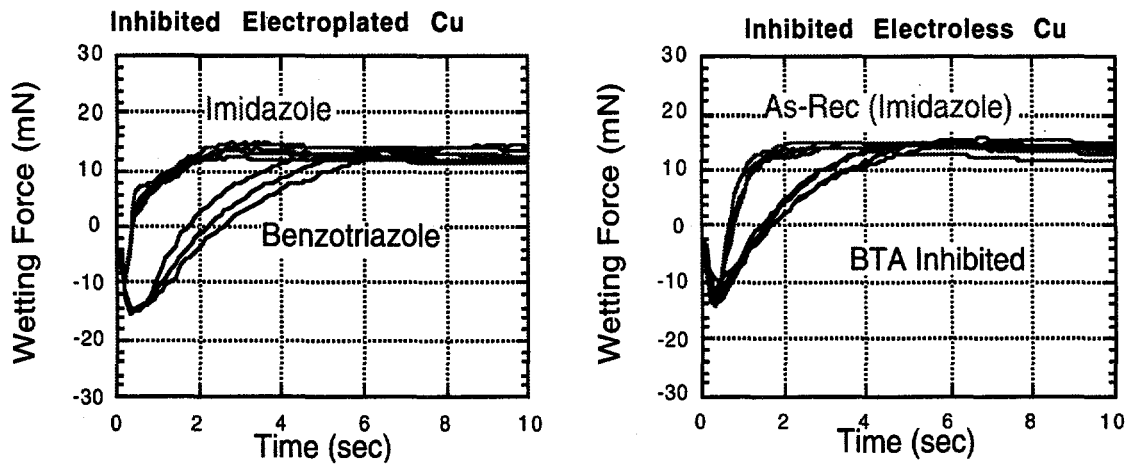


Figure 6. Effect of inhibitor on wetting balance behavior of copper.

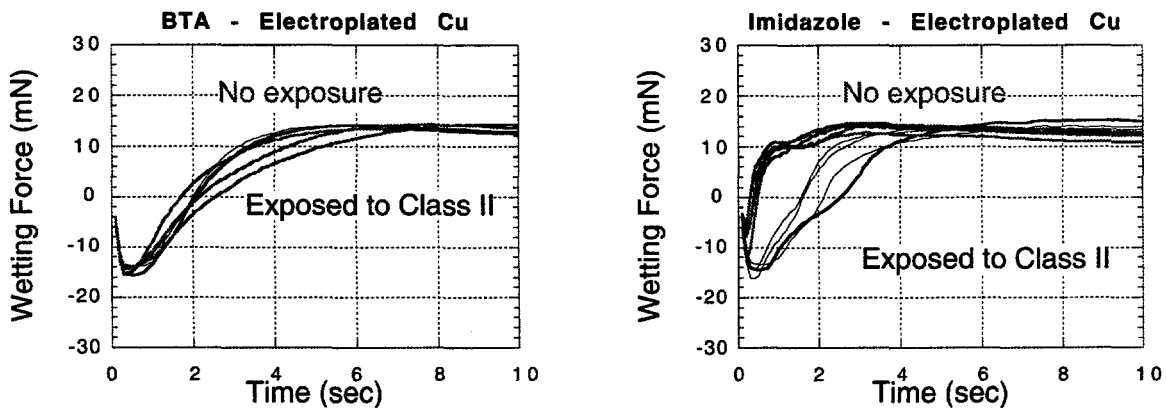


Figure 7. Effect of FACT exposure on wetting balance behavior of inhibited copper.

A compilation of results for these tests is presented in Figure 8. In this figure, wetting balance curves for etched copper, etched copper exposed in the FACT, and inhibited copper exposed in the FACT are presented. While the inhibitor does not retain the original solderability of the etched copper, both the BTA and IMD are effective in maintaining solderability after atmospheric exposure. Similar behavior was observed for both inhibitors, although the imidazole exhibited more scatter once the samples were aged. The IMD wetting curves exhibited a distinct plateau while the BTA curves were grouped quite closely, and displayed no break in the slope.

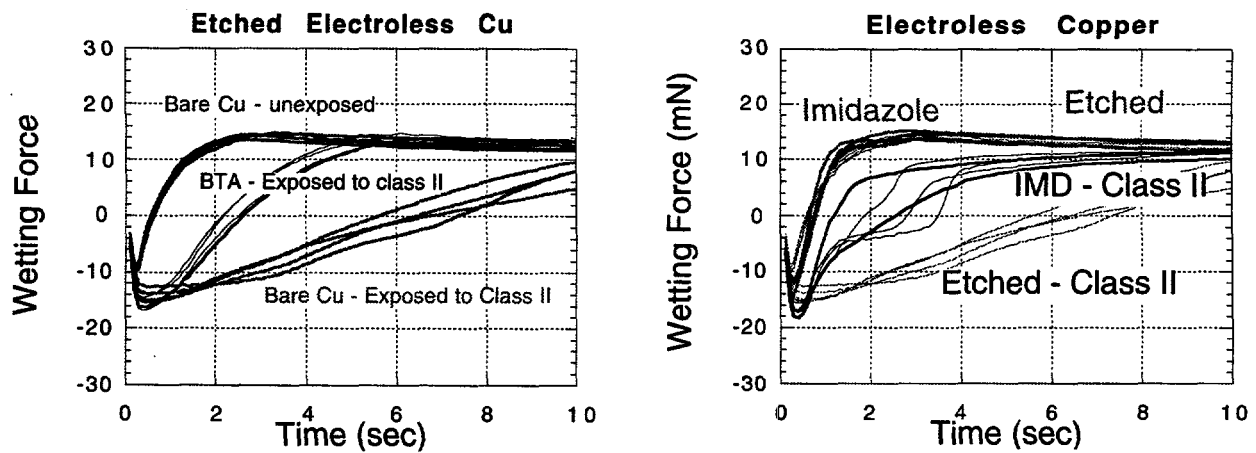


Figure 8. Wetting behavior for electroless Cu. Data for imidazole and benzotriazole coated copper are included.

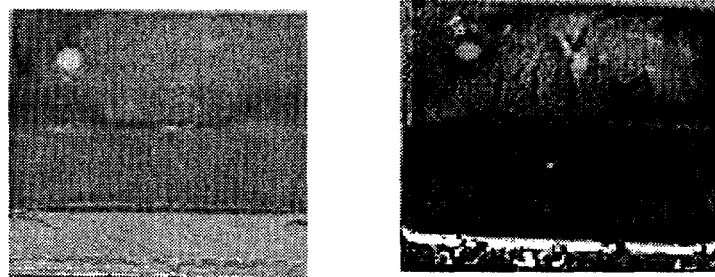


Figure 9. Optical photographs of Cu samples used in solderability tests. Sample on the left was protected with benzotriazole, while the sample on the right was not. Both samples were exposed to a class II environment followed by wetting balance tests.

In addition to wetting balance curves, optical images of the wetting balance samples provide some interesting data about the effect of inhibitors. Figure 9 shows optical photographs of typical samples. There are several features that should be pointed out:

1. The bare Cu sample is severely tarnished due to FACT exposure. The surface looks black and is not to be solderable.
2. The inhibited samples exhibit much less tarnish. The inhibitors have decreased the rate of attack of the copper in the Class II environment.
3. The bare copper sample does not wet. The small amount of solder present is only on the edge of the sample, with no real adhesion or wetting along the surface.
4. The inhibited sample wet very well. The meniscus is level and uniform, and the solder adheres very well to the copper surface

Thus it is clear, from both surface observations and wetting balance data, that organic inhibitors can be effective in preserving solderability. The inhibitor forms a complex with the surface which im-

pedes the corrosion process (probably by acting as a physical barrier to prevent water and gasses from contacting the surface). During the soldering process, the inhibitor must be removed to allow wetting of the Cu by the solder. At the solder temperatures the inhibitor copper complex is broken down and the inhibitor is removed, leaving an oxide free, clean copper surface. This surface is easily wetted by the molten solder.

It is clear from this study, that both imidazole and benzotriazole can be used in printed wiring board applications. They can be applied from an alcohol or aqueous solution, and can be applied quite easily. They are effective inhibitors for preventing corrosion, but still maintain solderability.

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The authors would like to acknowledge the assistance of G.A. Poulter, who performed the atmospheric corrosion exposure tests and C. Hernandez, who ran the wetting balance experiments. We would also like to thank George Wenger of AT&T who supplied the printed wiring boards, and the NCMS surface finishes team for input into the experimental study.

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