

## **PROTECTION OF CORROSION-SENSITIVE ARTIFACTS**

**J.P. Franey, G. Derkits, and D. Fleming**  
**Alcatel-Lucent**  
**Murray Hill, NJ, 07974, USA**

### **ABSTRACT**

Protection and preservation of corrosion-sensitive materials is a critical mission for many technologies, ranging from today's electronic industries, to forensic evidence, museum collections and archeological research organizations. Electronic components and assemblies will experience continued degradation upon continuous exposure to atmospheric corrosive environments. Forensic materials and artifacts may experience rapid and irreversible changes on exposure to ambient atmospheres. For electronics, some in-service corrosion mitigation is considered during design but degradation during storage and shipping is often ignored, especially for the repair cycle. Chemical coatings applied as protective layers on artifacts may adversely affect patina and destroy the chemical integrity of the surface. Using mixed flowing gas and temperature humidity stress environments, we have examined the protective effects of encapsulating copper, silver, and aluminum samples in bags made of Static Intercept reactive polymer material, without the addition of surface amendments, coatings, etc. We report sample preparation methods and reproducible quantified measurements of corrosion protection in the form of mass gain per area for protected and unprotected surfaces. We find that this preservation method greatly impedes the continuance of corrosive reactions keeping the reactive surfaces free of contaminating chemicals and corrosion, and intact and available for further study without time-dependant degradation.

### **KEY WORDS**

Corrosion, protection, temperature, humidity, stress, mixed flowing gas, packaging, Static Intercept, electronics, telecommunications, forensic evidence preservation, artifact preservation.

### **INTRODUCTION**

The present global business system involves the deployment of manufactured articles such as telecommunications electronic assemblies. These articles are manufactured in one country and may be stored, shipped, deployed, repaired, and redeployed across oceans and through a series of many other countries. Artifacts and such as paintings, sculptures and even materials gathered in evidence of a crime, can have similar uncalculated environmental stresses from many activities that can radically change

their characteristics. These activities may expose artifacts which have been exposed to the environment in service to further insult during shipping and storage. A question that arises from this is: “What is the best method for protecting already-exposed materials during this process?” Although many studies have been done examining the effects of corrosive environments on virgin materials, we are not aware of any study that attempts to simulate the effect of further exposure on already-damaged materials and to measure quantitatively the effectiveness of protective packaging. This study simulates the effect of transport, storage and redeployed materials, such as those which would occur in an analysis, repair, storage, or redeployment cycle. We use mixed flowing gas (MFG) and temperature-humidity (TH) accelerated stress environments to examine the effect of humidity and further environmental corrosion on artifacts and the effect of a simple protection method – storage in Intercept Technology™ bags – on the corrosion of samples of copper, silver, and aluminum. Prior studies<sup>1</sup> demonstrated the effectiveness of Intercept Technology packaging in preserving solderability of copper surfaces for as long as 17 years.

## EXPERIMENTAL PROCEDURE

Pure metal test coupons were used as test vehicles to quantify the amount of corrosion on exposed metal surfaces. The use of pure metal coupons is a well-established method of characterizing environmental corrosion<sup>2</sup>. We chose three metals typically found in electronic equipment and susceptible to corrosion: copper, silver, and aluminum. The use of copper as a calibration vehicle for calibration of mixed flowing gas chambers helps to tie the results back to standard tests such as the Telcordia GR-63 NEBS<sup>(1)</sup> test<sup>3</sup>. Silver has a different reaction profile from copper and also has a long history of use as a reaction monitor<sup>4</sup>. Aluminum corrosion in mixed flowing gas has not been reported in detail prior to this study. The coupons are made of pure metal foils (99.999% copper Alfa Aesar #42189, 99.998% silver Alfa Aesar #12126 and 99.99% aluminum Alfa Aesar #40760).

The metal foil was cut into 2cm x 5cm x 0.1mm test coupons. A series of five small holes in binary code were punched into coupons for identification and an additional hole for support. Prior to weighing, the coupons were cleaned in order to remove organic contamination and surface oxidation using the protocols listed in Tables 1 and 2. These cleaning procedures are somewhat different from those provided in ASTM and Telcordia standards, but we believe that they provide more reproducible and accurate results. In this study the copper coupons were designated Cu8, Cu9, Cu10 and Cu11, the silver coupons were designated Ag1, Ag2, Ag3, and Ag4, and the aluminum coupons were designated Al0, Al2, Al3, and Al4.

After cleaning and drying, each fresh coupon was weighed five times using a calibrated Mettler UMT2 microbalance. When using metal coupons as test vehicles, it is critical to minimize the degree of surface oxidation and contamination. To this end, the coupons are cleaned, dried, and weighed on the same day and handled only with clean plastic tweezers. Immediately after weighing, the coupons were stored in Static Intercept® (SI) bags to avoid extraneous oxidation or contamination. The protective bags used for storage were composed of the same material used as the protective packages in the environmental tests, which is available commercially under the trade name Static Intercept<sup>(2)</sup>.

A Mettler UMT2 microbalance was used to measure the weight of the individual coupons before and after exposure. The Mettler UMT2 microbalance is calibrated annually using NIST traceable standards. The capacity of the Mettler UMT2 balance was 2100 mg and well suited for the coupons that weighed from 1000mg (silver coupons) to 240mg (aluminum coupons). The readability and repeatability

---

<sup>(1)</sup> NEBS is a trademark of Telcordia Technologies, Inc.

<sup>(2)</sup> Static Intercept is a trademark of Engineered Materials, Inc.

of the Mettler UMT2 microbalance itself was 0.1 $\mu$ g and 0.25  $\mu$ g respectively. Prior to weighing, the room temperature and humidity were recorded. The precision and accuracy of the microbalance was checked by weighing a NIST-traceable platinum standard five times in auto mode. The standard used weighed 838 mg, a weight comparable to that of the coupons. For our work extending over two months, the standard deviation of the weight of the platinum standard was 1.7 $\mu$ g (2ppm).

**TABLE 1**  
**CLEANING PROCESS FOR Cu AND Ag COUPONS**

Step	Instructions
0	Handle coupons only with clean plastic tweezers.
1	Immerse all coupons for 5 minutes in a beaker of acetone in an ultrasonic bath.
2	Rinse coupons 10-60 seconds in Isopropanol.
3	Rinse coupons 10-60 seconds in deionized (DI) water.
4	Place each coupon one at a time into 5 vol% HNO <sub>3</sub> /DI H <sub>2</sub> O. Surface oxide should be removed immediately. You should see the color of the coupon change to look like a “bright new copper penny” as the coupon drops to the bottom.
5	Remove coupon from acid and place in running overflow DI (or distilled) water for 1 minute.
6	Rinse coupons 10-60 seconds in Isopropanol
7	Dry coupons in a vacuum oven (60 C) and vent with nitrogen flow for approximately 1 hour.

**TABLE 2**  
**CLEANING PROCESS FOR Al COUPONS**

Step	Instructions
0	Handle coupons only with clean plastic tweezers
1	Immerse all coupons in deionized (DI) water in a glass beaker. Place beaker into ultrasonic cleaning bath with power on for 20 minutes.
2	Next etch coupons with H <sub>3</sub> PO <sub>4</sub> acid diluted to 45 wt-% with distilled water. Immerse the coupons in the H <sub>3</sub> PO <sub>4</sub> acid which is contained in a clean glass beaker. Place the beaker containing the coupons and acid in a powered on 45-50C ultrasonic bath for 35 minutes. This treatment removes the existing aluminum surface oxide layer along with contaminants and exposes a fresh aluminum surface which will subsequently oxidize under ambient conditions.
3	Remove coupon from acid and place in running overflow DI (or distilled) water for 1 minute.
4	Rinse coupon 10-60 seconds in acetone followed by a second rinse for 10-60 seconds in Isopropanol.
5	Dry coupons in a vacuum oven (60 C) and vent with nitrogen flow for approximately 1 hour.

The experiments were designed to provide contrasts between protected (inside SI bag) and unprotected (exposed to environment) as the coupons were exposed to stress environments of different severity ranging from laboratory air, accelerated Temperature (40C) and Humidity (85%RH) stress, and Mixed Flowing Gas in excess of Class III or NEBS outdoor conditions.

**TABLE 3**  
**CHARACTERISTICS OF TEST STRESS CONDITIONS**

	MFG1	Air (P)	Air (U)	TH(P)	TH(U)	MFG2(P)	MFG2(U)
H2S (ppb)	2000	4	4	4	4	2000	2000
SO2 (ppb)	200	3	3	3	3	200	200
NO2 (ppb)	200	3	3	3	3	200	200
Cl2 (ppb)	20	1	1	1	1	20	20
RH (%)	75	65	65	85	85	75	75
T ( C )	40	22	22	35	35	40	40
Hours	72	96	96	72	72	24	24

After sample preparation and initial weighing, all of the coupons were exposed in a mixed flowing gas chamber. All coupons were weighed again after each exposure and the resulting weight was used as the base weight to measure mass gain in further exposures. Coupons to be protected were placed loosely into Static Intercept bags which were sealed at the open end by thermal seam sealing. Coupons were exposed to stress environments so that contrasts between protected and unprotected status were available for each stress, with the exception of copper, for which the MFG exposure received equal weight to allow copper to serve its usual role as a standard. The exposure history of all of the coupons is shown in Table 4. In Tables 3 and 4: Process 0 is the preparation step; Process 1 is the initial MFG exposure; Process 2 is laboratory air exposure; Process 3 is the Temperature-Humidity exposure; and Process 4 is the second MFG exposure; within parentheses “P” indicates that the coupon is protected inside SI bag and “U” indicates that the coupon is unprotected with a surface exposed to the stress environment.

**TABLE 4**  
**EXPOSURE HISTORIES OF COUPONS**

Sample	Prep	MFG1	Air (P)	Air (U)	TH(P)	TH(U)	MFG2(P)	MFG2(U)
Cu8	0	1	2P				4P	
Cu9	0	1	2P				4P	
Cu10	0	1	2P			3U		4U
Cu11	0	1		2U		3U		4U
Ag1	0	1	2P		3P			
Ag2	0	1	2P				4P	
Ag3	0	1		2U		3U		4U
Ag4	0	1	2P			3U		4U
Al0	0	1	2P		3P			
Al2	0	1	2P				4P	
Al3	0	1	2P			3U		4U
Al4	0	1		2U		3U		4U

## RESULTS

All metals showed significant weight gain in mixed flowing gas exposure. The mean weight gain per area of the Cu coupons in the initial MFG exposure was 164  $\mu\text{g}/\text{cm}^2$ . The Telcordia GR-63 NEBS standard uses 20-30  $\mu\text{g}/\text{cm}^2$  per year as the estimated corrosion of standard copper coupons in an outdoor environment in the North Atlantic Region (NAR)<sup>3</sup>. This places the initial exposure as roughly

equivalent to 5-8 years of typical outdoor exposure in NAR. The mean weight gain of copper coupons in the second MFG exposure was 84  $\mu\text{g}/\text{cm}^2$ , which is equivalent to a 3-4 year NEBS outdoor exposure. As reported elsewhere<sup>5</sup>, environmental conditions in other parts of the world may be considerably more corrosive than in NAR, so these weight gains may be equivalent to a much shorter exposure time in more severe environments.

**TABLE 5**  
**AVERAGE MASS GAIN FOR UNPROTECTED COUPONS IN PRELIMINARY MIXED FLOWING GAS STRESS EXPOSURE**

<b>Metal</b>	<b>DMPA [<math>\mu\text{g}/\text{cm}^2</math>]</b>
Cu	164
Ag	10.7
Al	8.2

Average mass per area gains (in  $\mu\text{g}/\text{cm}^2$ ) for protected and unprotected samples in post-exposure temperature and humidity (TH) stress are shown in Table 6 and for MFG stress are shown in Table 7.. Note the presence of apparent negative mass gains. These values are well above the error of measurement for the Mettler balance considered as an instrument alone, however additional contributions to error are present in samples which have been corroded to a significant degree, as these have, due to the corroded surface, which can exchange moisture and particles with the environment. This raises the range of error associated with corroded samples to perhaps as great as 1  $\mu\text{g}/\text{cm}^2$ , which is still well below the gains recorded for the exposed samples in the MFG test.

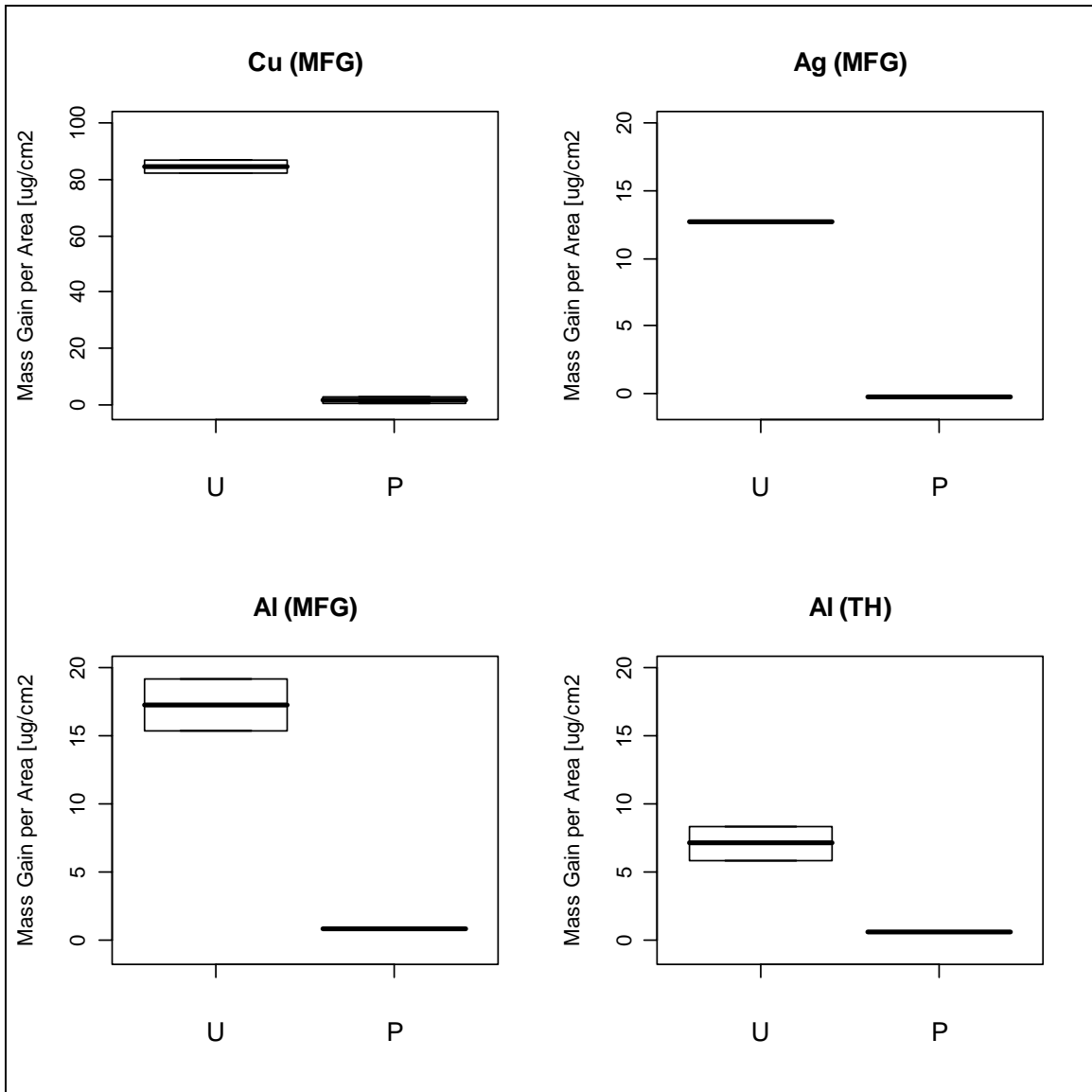
**TABLE 6**  
**AVERAGE MASS GAIN FOR PROTECTED AND UNPROTECTED COUPONS IN TEMPERATURE-HUMIDITY STRESS EXPOSURE**

<b>Metal</b>	<b>Status</b>	<b>DMPA [<math>\mu\text{g}/\text{cm}^2</math>]</b>
Cu	U	0.087
Cu	P	NA
Ag	U	-0.087
Ag	P	-0.36
Al	U	7.1
Al	P	0.6

**TABLE 7**  
**AVERAGE MASS GAIN FOR PROTECTED AND UNPROTECTED COUPONS IN SECOND MIXED FLOWING GAS STRESS EXPOSURE**

<b>Metal</b>	<b>Status</b>	<b>DMPA [<math>\mu\text{g}/\text{cm}^2</math>]</b>
Cu	U	84.3
Cu	P	1.81
Ag	U	12.64
Ag	P	-0.22
Al	U	17.3
Al	P	0.87

Only Al coupons showed a significant weight gain in response to Temperature-Humidity stressing. All three metals showed a highly-significant response to MFG stress.



**Figure 1 - Mass gain per unit area in micrograms per square centimeter, for Protected (P) and Unprotected (U) samples of Cu, Ag, and Al in mixed flowing gas and temperature-humidity environments.**

## CONCLUSIONS

We have shown that all three metals Cu, Ag, and Al are protected to a significant degree by Static Intercept packaging in MFG simulations of harsh environments equivalent to several years of exposure in the field. We have shown that Al samples corrode significantly in MFG environments and continue to corrode in TH environments, unless protected by a barrier such as Static Intercept®. The results demonstrate a cost-effective method that can protect already-deployed artifacts from environmental corrosion during the shipping-storage-repair-redeployment cycle. We believe that these results have strong implications for shipping and storage of electronic components used in the telecommunications. These results may also be of significant interest to other industries which require protection of artifacts from environmental effects, including museums and archeological excavations

and potentially for other applications which require the preservation of reactive materials, such as forensic evidence.

## DISCUSSION

A great part of the literature on the preservation of artifacts comes from the literature of museum curatorship<sup>6</sup>. A different niche literature, especially devoted to aluminum, exists in the nuclear fuel industry<sup>7</sup>. Although there is a substantial body of literature<sup>8</sup> concerning the preservation of newly-manufactured electrical products, we have not found any significant literature on the preservation of objects which have already suffered damage from environmental exposure. This type of damage frequently occurs as components and sub-assemblies of final product are manufactured, stored, and/or shipped from various global sites prior to final deployment at the end user's site. This paper is an attempt to address that gap in the literature and provide experimental evidence that the preservation of electrical and other complex products can be achieved with a non-invasive, low-cost packaging approach.

## ACKNOWLEDGEMENTS

We gratefully acknowledge the support of Marc Benowitz.

## REFERENCES

1. Franey, J. and D-M. Sutton. 2006. "Static Intercept\* Technology: A New Packaging Platform for Corrosion and ESD Protection," Bell Labs Technical Journal, 11(3):137-146
2. ASTM International, "Standard Test Method for Calibration of Atmospheric Corrosion Test Chambers by Change in Mass of Copper Coupons," ASTM B 810-01a, Nov. 10, 2001.
3. Telcordia Technologies, "NEBS™ Requirements: Physical Protection" Generic Requirements GR-63-CORE, Issue 2, April 2002, Method 5.5.2.
4. Rice, D., P. Peterson, E. Rigby, P. Phipps, R. Cappell, and R. Tremoureux, "Atmospheric Corrosion of Copper and Silver," J. Electrochem. Soc. 128(2):275-284.
5. Derkits, G., J. P. Franey, and W. D. Reents. 2006. "Biased Mixed Flowing Gas Testing for World Class Reliability," Bell Labs Technical Journal, 11(3):105-120.
6. Scott, D., 1990, "Bronze Disease: A Review of Some Problems and the Role of Relative Humidity", J. American Institute for Conservation, 29(2):193-206.
7. Peacock, H., R. Sindelar, P. Lam, T. Murphy, 1994, "Experiments for Evaluation of Corrosion to Develop Storage Criteria for Interim Storage of Al", Proceedings of the Topical Meeting on DOE Spent Nuclear Fuel - Challenges and Initiatives, Salt Lake City, Utah, December(1994)pp76-82, WSRC-MS-94-0564.
8. Tullmin, M. and P. Roberge, 1995, "Tutorial: Corrosion of Metallic Materials", IEEE Transactions on Reliability, 44(2):271-279.