

**Corrosion of**  
**Electronic**  
**and**  
**Magnetic**  
**Materials**

**Phillip J. Peterson**

EDITOR



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# *Corrosion of Electronic and Magnetic Materials*

*Phillip J. Peterson, editor*

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# Overview

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Modern civilization has an insatiable appetite for ever faster and improved communication plus a never-ending desire to store, retrieve, and manipulate information no matter where we are, whether in our offices, stuck in a traffic jam on the freeway, or sunning ourselves on the beach. This desire and appetite has driven the use of electronic and magnetic materials to dimensions that are rapidly approaching atomic units, to include exotic materials for which little if any corrosion experience exists, and to survive hostile environments. Through global competition, these products must be produced at decreasing costs, increasing reliability, and decreasing development time.

The shrinking size of our electronic and magnetic devices have forced us to take a closer look at corrosion. We must extend our limits for what we call corrosion. Is Pourbaix's  $10^{-6}$  limit still valid? Is what we used to consider mild inconsequential tarnish now to be considered devastating corrosion? This new closer look at corrosion is reflected in the papers of Rickett and Payer, Goodson and Chang, and Hadad and Pizzo.

In the past, engineers have shied away from using materials they had no experience with or for which they could not find corrosion data. At present and especially in the future, we cannot afford to do this and stay competitive. We must either produce our own corrosion data and/or encourage and facilitate publication of corrosion studies of new materials such as those by Kim and Camp; DeBold, Masteller, Werley, and Carpenter; and Lee and Stevenson.

Computer power that only a few years ago was found exclusively in clean, air-conditioned rooms that would rival medical operation rooms can now be found on laps by the seashore. Telephones now have such scanty protective covers that even Superman is taken back. Today we carry on our wrists through rain, snow, swimming pools, and saunas sophisticated electronic devices that would make Dick Tracy envious. And yet, thanks to global competition, many of these devices are so cheap we would rather discard them than replace their batteries. In the past, sophisticated electronic and magnetic materials were protected in hermetically sealed packages, a costly overprotection for most applications but requiring little knowledge of either the environment or its corrosive effects on these materials. But now, to be cost competitive, we must carefully define what is just-sufficient-protection for our products to survive the environment in which they are to be used. It is work like that of Schubert, Sproles, Setchell, and Yee and Bradford that enable cost competitiveness to be achieved without sacrificing product reliability.

To ensure the reliability of products with new materials or even old materials with new packaging, environmental exposure tests are required. From the pressures of competitive time development, it is desirable for many of these exposure tests to be accelerated and their results made available at the time the new product is introduced in the marketplace. To do this, pre-agreed upon tests accepted by vendors, manufacturers, and customers must be in place. It is here where ASTM will play an important role in the development of new electronic and magnetic materials.

*Phillip J. Peterson*

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## Corrosion-Resistant Outdoor Electronics

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**REFERENCE:** Schubert, R., Veca, A., and Fischer, E., "Corrosion-Resistant Outdoor Electronics," *Corrosion of Electronic and Magnetic Materials, ASTM STP 1148*, P. J. Peterson, Ed., American Society for Testing and Materials, Philadelphia, 1992, pp. 1-10.

**ABSTRACT:** The operating telephone companies are committed to assuring reliable and continuous quality telephone service. Environmental durability must be designed into the components of the electronic coin telephone that is often located in uncontrolled environments and in areas of continuous exposure to corrosive pollutants. To observe and quantify the effect of the environmental pollutants on coin telephone equipment, functional but unboxed electronic printed circuit board assemblies, a fully assembled, unboxed electronic chassis and coin acceptor, and a fully housed electronic chassis and coin acceptor were placed in a chamber and exposed to a pollutant-containing environment along with copper, nickel, and electroplated gold control coupons. The test pollutant atmosphere was a Battelle Laboratories Class III atmosphere consisting of air at 30°C and 70% relative humidity with H<sub>2</sub>S, Cl<sub>2</sub>, and NO<sub>2</sub> at 100, 20, and 200 ppb, respectively. We report the results of Auger electron spectroscopy with Ar<sup>+</sup> ion depth profiling that was done on various electronic components from housed and unboxed circuit packs and the control coupons. In general, corrosion film thicknesses on circuit components were less than coupon film thicknesses. This is attributed to the circuit pack geometry and component shrouding. A theoretical model supports the experimental results. Repeated functional testing at 95% relative humidity of both the housed coin telephone and unboxed assemblies was performed after exposure in the polluted atmosphere. After exposure, all circuits performed according to specification with respect to laboratory central office equipment and a fully active coin operation telephone line.

**KEY WORDS:** corrosion, contacts, electronics, tin, gold, copper, nickel, nitrogen dioxide, chlorine, hydrogen sulfide, flowing mixed gas testing

Customers expect reliable and continuous quality telephone service, and the Bell operating companies (BOCs) are committed to assuring such service. Providing this level of service requires that environmental durability be designed into the components of coin telephone stations to assure reliability, to minimize the cost of field repairs, and to increase revenue. Electronic coin telephone station equipment is often located in uncontrolled environments and in areas of continuous exposure to corrosive pollutants with the external telephone housing acting as the primary barrier to the expected pollutants. The pollutant compounds of interest include NO<sub>x</sub>, O<sub>3</sub>, SO<sub>x</sub>, H<sub>2</sub>S, and Cl-containing molecules in urban, outdoor, street-level environments [1-3]. Furthermore, the equipment must tolerate various salts and organic vapors at relative humidities as high as 100% and operate over a temperature range of -34 to +66°C.

A number of simulated environmental tests already exist, i.e., salt fog [4], sulfur dioxide [5], humidity, and temperature cycling [6], as well as numerous modifications to these tests. These tests are of questionable use for general atmospheric corrosion for electronic devices. For example, the salt fog test simulates an atmosphere found primarily on the seacoast or on

<sup>1</sup> Bellcore, Red Bank, NJ 07701.

<sup>2</sup> Mars Electronics International, Inc., West Chester, PA 19380.

<sup>3</sup> NYNEX Enterprises, New York, NY 10001.

board seagoing vessels. The sulfur dioxide ( $\text{SO}_2$ ) test uses concentrations greatly in excess of normal atmospheres and does not include any chlorine-containing gas. Humidity and temperature cycling do not include any specific pollutants. The Battelle Laboratories flowing mixed gas test [7] overcomes the above objections by using chlorine ( $\text{Cl}_2$ ), hydrogen sulfide ( $\text{H}_2\text{S}$ ), and nitrogen dioxide ( $\text{NO}_2$ ) gases at the part per billion (ppb) level.

Most people are familiar with the outside of a coin-operated telephone terminal. It is an enclosure which has few accesses for the intake or exhausting and exposure of the electronic components to flowing pollutant gases. However, there are flow paths that allow the housing to intake or exhaust gases caused by atmospheric temperature and pressure changes and wind-induced venturi effects. These accesses are located at the rear of the terminal housing for mounting and wiring purposes, in the front by the coin slot, the coin return chute, and the vault door, and at the interface between the upper and lower housing. In addition, the system components are fully exposed to the outside street atmosphere during short periods of time while the upper housing is removed for maintenance.

The internal housing volume is approximately 10 L, and the internal components' volume utilizes approximately 6 L. The remainder is free space. The internal surface area of the covered electronic chassis and coin chute exposed to the enclosed atmosphere (not including the inner housing walls) is approximately  $1900 \text{ cm}^2$ , of which  $1300 \text{ cm}^2$  is plastic and the remainder is printed circuit board and metal chassis. Other internally exposed surfaces were not assessed. However, it is noted that these internal surfaces appear to be bare (and unpassivated) metal consisting of carbon steel and brass, except for paint overspray on the inside of the upper and lower housings. The major portions of the external upper and lower housing surfaces are painted, and various external components such as the switch hook, key-pad dial bezel, coin return door, handset retainer, and instruction placard trim and bezels are chromium plated. However, it is the electronics which are of prime importance with regard to corrosion.

In this paper, we report the results of accelerated atmospheric corrosion testing of the electrical components from electronic coin telephones. Surface analysis shows substantial corrosion occurring on copper surfaces and gold electroplated surfaces, but *minimal corrosion on tin or shrouded surfaces*. All electronic components worked as specified after the exposure.

## Experiments

The equipment subjected to the flowing mixed gas corrosion chamber (FMGCC) test discussed below were Mars Electronics modular retrofit components and a complete system for coin-operated telephone sets.<sup>4</sup> The retrofit system (LES-100-WE) consists of an electronic communication and control chassis and an electronic coin chute. The sample materials for corrosion testing were randomly selected from production output that were manufactured according to Mars' standard processes and specifications. Then they were acceptance tested according to established test protocols which are proprietary.

The printed circuit boards were manufactured using FR4 material, subtractive process, and solder mask over print wires. This process meets surface insulation resistance requirements in accordance with established measuring procedures [8]. Printed circuit board layout and design are consistent with various industry standards and recommended techniques [9].

The separable connectors used to interconnect the circuit boards and components are typically AMPMODU styles manufactured by AMP. These are made from a copper alloy strip which is nickel and tin plated in certain areas and then selectively gold plated in the contact

<sup>4</sup> These new units were designed to convert the existing analog coin telephone to a centrally diagnosable, digital telephone.

regions. Finally, the strip is stamped and formed into the individual contacts. This process leaves exposed edges of copper alloy from the stamping operation at several locations.

Other than assuring printed circuit board cleanliness prior to and subsequent to manufacture, no special processing or substances are used to specifically guard against or retard the possible effects of exposure to aggressive atmospheric contaminants. Cleanliness of the printed circuit boards is established by using recognized industry cleaning methods after assembly, i.e., a 104°C CFC-6% methanol process suitable for removal of solder flux or temporary solder resist materials. Cleanliness is maintained throughout the assembly and test process by operators wearing protective gloves to avoid the deposition of residues resulting from perspiration.

In order to gain the maximum amount of information from the test samples, the experiment was arranged to expose a variety of electronic components at different stages of assembly, as well as multiple control coupons. A set of individual printed circuit boards with a full complement of components, a set of printed circuit boards assembled as a chassis mount pack, a mount pack assembled into a chassis without covers, a completed chassis with covers, a chassis installed in a lower coin-operated telephone housing without upper housing, and a completely assembled coin-operated terminal as would be placed into operation in the street environment were all exposed in the FMGCC. In total, the electronic components sample consisted of seven sets of electronic printed circuit boards exposed in a manner to range from minimum protection to maximum protection from a corrosive mixed gas atmosphere. Three types of control coupons, electroplated acid hard gold over sulfamate plated nickel over copper, pure copper (Cu), and pure nickel (Ni), were placed inside the assembled housing, on the housing surface, and at several other free-standing locations near the circuit packs. The control coupons' function was to provide visual verification that corrosion was proceeding normally during the test [7].

Each set of boards was assembled into a complete chassis prior to exposure, and the chassis was tested for full operation and functionality on a live coin-operated telephone line and then disassembled to the necessary state in preparation for the FMGCC test.

Individual circuit boards, assembled components, a fully assembled, working, housed coin telephone, and metal control coupons were all tested together in Battelle Laboratories' (Columbus, OH) FMGCC [7] for seven days. The exposure atmosphere was 100 ppb H<sub>2</sub>S, 20 ppb Cl<sub>2</sub>, and 200 ppb NO<sub>2</sub> in air at 30°C and 70% relative humidity (RH); this corresponds to a Class III environment [7]. Chamber air was exchanged six times per hour. Pollutant gases were stabilized prior to insertion of the samples; all conditions were monitored continuously except Cl<sub>2</sub>, which was only verified at the beginning and the end of the experiment. All component sets were electrically isolated and spatially separated by at least 5 cm. After exposure, all electrical components were functionally tested to manufacturing specifications.

The process of functionally testing the exposed sets of electronics consisted of three phases: (a) under ambient laboratory conditions of 22°C and 56% RH after FMGCC exposure; (b) after equilibrating for 24 h in an environment of 60°C and 95% RH after (a); and (c) after equilibrating with the ambient laboratory conditions of 25°C and 54% RH subsequent to the 60°C and 95% RH test.

In addition to the three completely assembled sets, i.e., a set in the complete housing, a set in the lower housing without upper housing, and a set in the complete chassis with covers but no housing, the remaining exposed free-standing printed circuit boards were assembled into chassis in order to facilitate operational tests.

The coin telephone operates from power supplied to the "tip-ring" telephone terminals from the telephone central office at the specified telephone line voltage ranging from 42.5 to 52.5 Vdc and telephone loop currents ranging from 23 to 80 mA. No telephone line power is required in the "on-hook" condition.



The objective of the operational tests subsequent to exposure was to assure that the performance and functions of the Mars' Modular Electronic Retrofit System satisfied the specified operating requirements. This included: (1) receive, transmit, and side tone audio quality; (2) electronic data acquisition, processing, and retention; (3) transmission of station status, alarms, and scheduled reports; (4) dual tone multifrequencies and tone quality; (5) coin tone quality and frequencies; (6) coin acceptance, central office coin collection, and coin return. These specification values are listed in Table 1. Other properties tested were dielectric withstand, electrostatic discharge immunity, and the on-hook/off-hook impedances [10]. These functions all operate on a voltage of 6.8 to 7.0 V.

After FMGCC exposure and electronic testing, the components were inspected and analyzed by Auger electron spectroscopy (AES). A Perkin-Elmer PHI 600 spectrometer was used with an 80-namp, 10-keV electron beam used in the spot mode for analysis. Depth profiling was done with a 3-keV argon ion ( $Ar^+$ ) beam with an effective sputtering rate in silicon dioxide ( $SiO_2$ ) of 9.1 nm/min. For some thicker films, the sputtering rate was increased to 13.5 nm/min. No cleaning of the samples was done prior to analysis. No analysis was done in visible scratches, wear marks, or debris. Areas chosen for analysis were considered typical of the surfaces, for both exposed and unexposed samples.

## Results

The electroplated acid hard gold over sulfamate plated nickel over copper, pure copper, and pure nickel control coupons showed different degrees of corrosion depending on whether they were exposed in a free-standing position or within the coin telephone housing, as expected. Those samples exposed within the housing showed no visible corrosion. Figure 1 is a photograph of plated gold (Au) samples; the bright Au sample on the right was mounted inside of the housing, and the corroded sample on the left was mounted directly on the outside of the housing. Clearly, substantial pore corrosion occurred on the sample outside of the housing. Both the Ni and Cu samples exposed on the outside of the housing had turned black after the seven-day exposure, whereas the Ni and Cu coupons inside the housing showed no evidence of corrosion. Thicknesses of the corrosion films on the control coupons are given in Table 2 and were determined by coulometric reduction. The corrosion films on unprotected samples were sufficiently thick that no AES depth profiles were obtained.

The upper and lower housings were serviceable units that had prior field usage for an unspecified period of time. On areas where there were scratches in the painted surfaces, the scratches appeared to be blackened subsequent to exposure. No analysis was performed on the housings.

Although no specific analyses were done on any of the nonmetallic surfaces after the seven-

TABLE 1—Some electronic functions and typical requirements.

Function	Examples	Specifications
Audio quality and loudness	Transmit, receive, side tones	Over 4.5 km with 26 AWG wire, $\pm 50$ dB loudness
Digital data	Acquisition, retention, alarm/report	1200/2400 Baud
Analog data	Coins, dialing, voice	Frequency, $\pm 8$ Hz Amplitude, $< 10$ dBm loss Timing, tens of ms

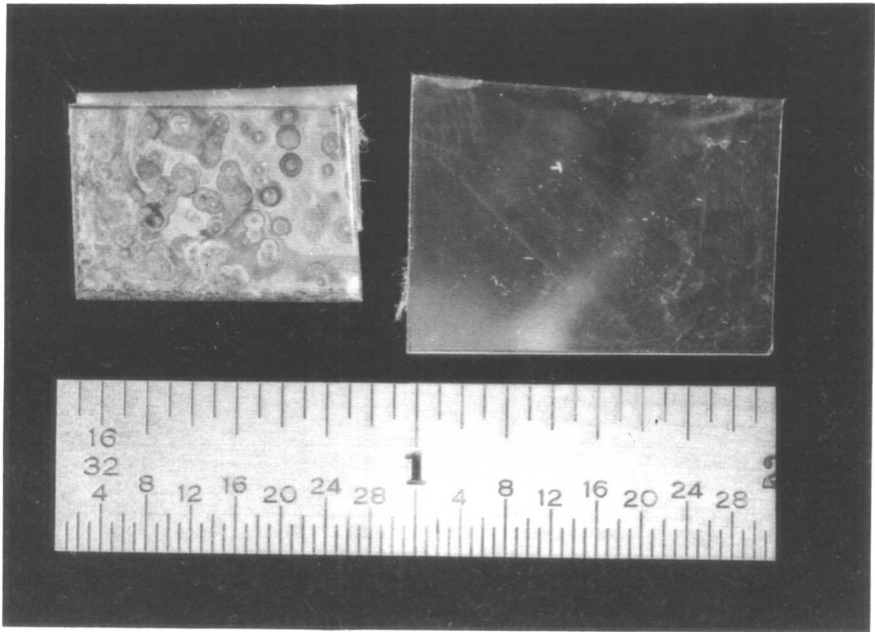


FIG. 1—Porous gold plate control coupons exposed for seven days in the FMGCC. The sample on the left was inside the coin telephone housing, and the sample on the right was on the outside surface of the housing.

day FMGCC exposure, visual inspection did not show any cracking, crazing, discoloration, or delamination. These surfaces will not be discussed further.

Visual inspection of the exposed tinned electrical components showed minimal corrosion. Exposed, unhoused tin surfaces showed a dulling and slight whitening as compared to the exposed, housed tin (Sn) surfaces, which retained their smooth and bright finish. Exposed, unhoused electroplated Au surfaces on some DIP lead frames had sufficient corrosion on the surface such that they appeared to be made of Cu.

A typical AES analysis of a Sn surface is shown in the differentiated spectrum in Fig. 2. Sn is the major component with lesser amounts of oxygen and carbon and with traces of sulfur and chlorine, which can all be attributed to typical adsorption of air components. Ar<sup>+</sup> depth profiling of this spot indicates that the surface contamination is less than 5 nm thick, i.e., the

TABLE 2—Equivalent film thicknesses on Cu control coupons.

Exposure Time, h	Location	Average Film Thickness, nm
48	Chamber	266
96	Chamber	377
145	Chamber	454
168	Chamber	605
168	On housing	600
168	In housing	33
192	Chamber	653

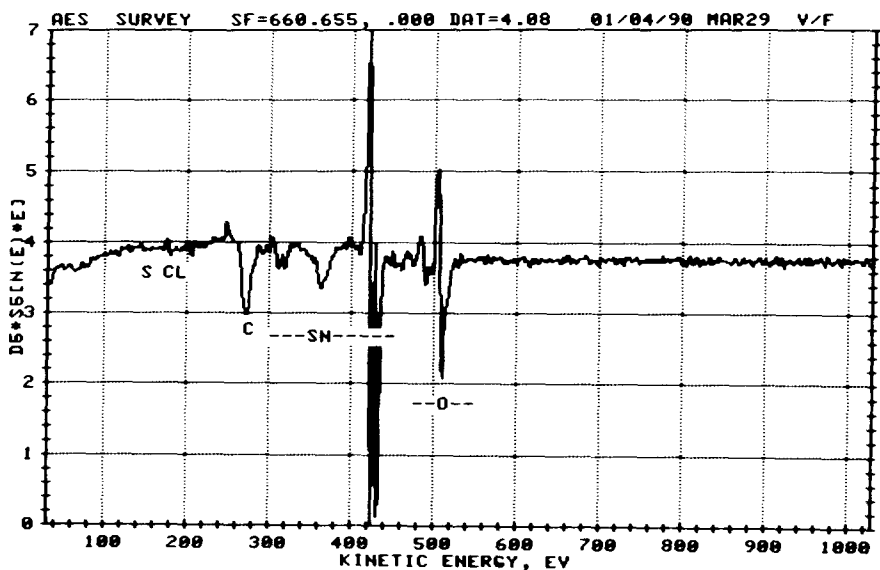


FIG. 2—A typical AES differentiated spectrum of a tin surface which had been exposed in the FMGCC for seven days. The surface contaminants are only in the uppermost 5 nm.

oxygen (O) and carbon (C) decreased to < 50 at% and the Sn signal increased to > 50 at% in less than 30 s of sputtering. These results are typical of both the housed, exposed samples and the unhoused, exposed samples.

Unhoused, exposed electroplated Au surfaces on DIP lead frames were sputter etched for over 120 min with no decrease in the Cu signal. Figure 3 is a survey spectrum of the sputtered area after 120 min of bombardment and shows mostly Cu with lesser amounts of sulfur (S), chlorine (Cl), C, and O; the strong Au peak at 69 eV is not visible. This corresponds to an equivalent thickness of  $\text{SiO}_2$  of > 1600 nm. Unexposed and exposed, but housed, electroplated Au lead frames both show a trace of Cu, which is only present in less than the top 20 nm of the surface. The AES survey shown in Fig. 4 was recorded after 4 min of sputtering; only Au is seen.

A full connector contact is shown in Fig. 5; the photo was taken using a scanning electron microscope after exposure and testing, removal from the polymer housing, and unfolding of the formed contact. On the fully exposed circuit boards, heavy corrosion occurred on the leading edge of the contacts at the open end (Areas A in Fig. 5), i.e., opposite the end where it was soldered to the circuit board. Areas A contain exposed Cu alloy from the stamping operation during manufacture. Areas B are primarily Ni plated and Areas C are primarily Au plated. Visible edges D are also exposed Cu from the stamping operation, but no significant corrosion is seen. The particles seen in Areas C are primarily Sn, which is also the surface material of the left-hand edge of the contact and the section where it is soldered to the circuit board. Energy dispersive X-ray analysis of the corroded edge, which was at the opening of the assembled contact and was exposed after the stamping operation, showed Cu, Cl, O, and S. No significant corrosion was observed in the Au contact region, nor was there any significant corrosion along the Cu alloy edge parallel to the contact edge, which was also exposed after the stamping operation.

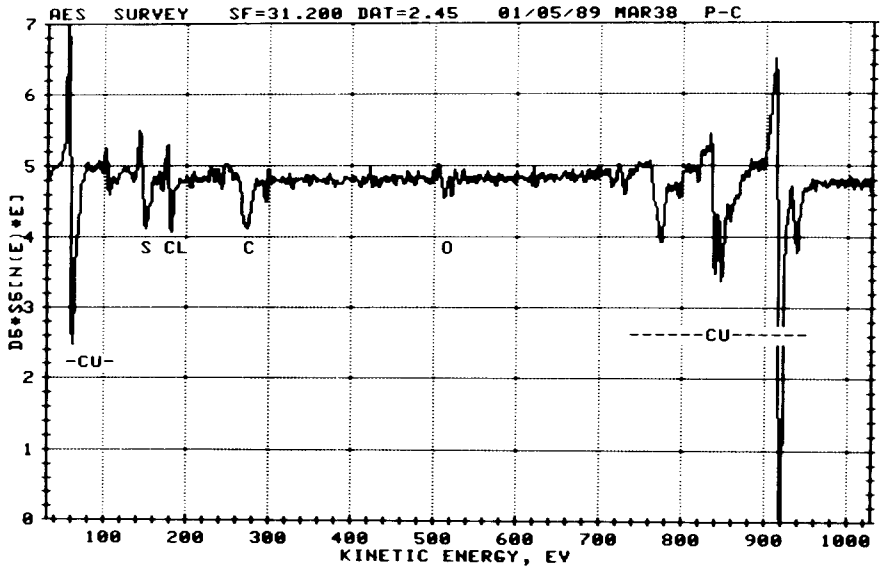


FIG. 3—A survey spectrum of an unhooded, exposed plated Au surface after 120 min of sputtering. The large low energy peak is the 60-eV Cu peak and not the 69-eV Au peak.

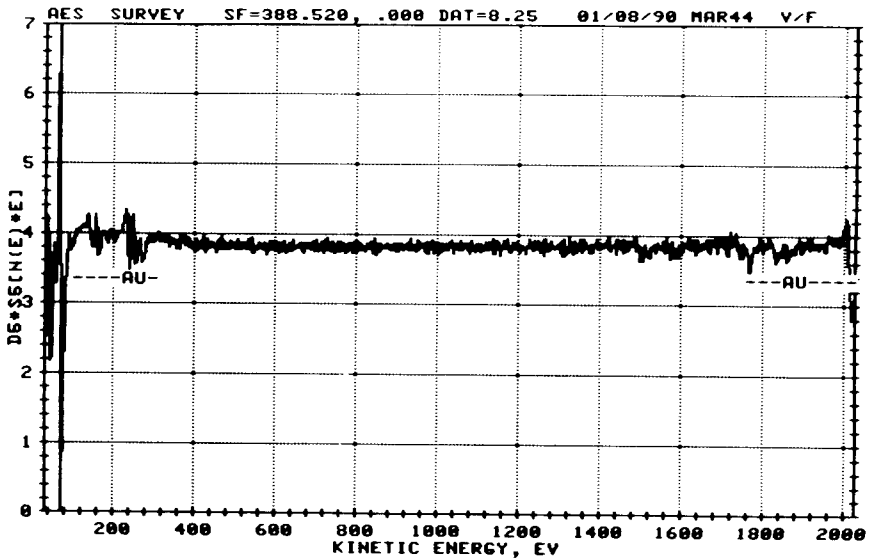


FIG. 4—An AES survey spectrum of an exposed, but hooded plated Au surface.

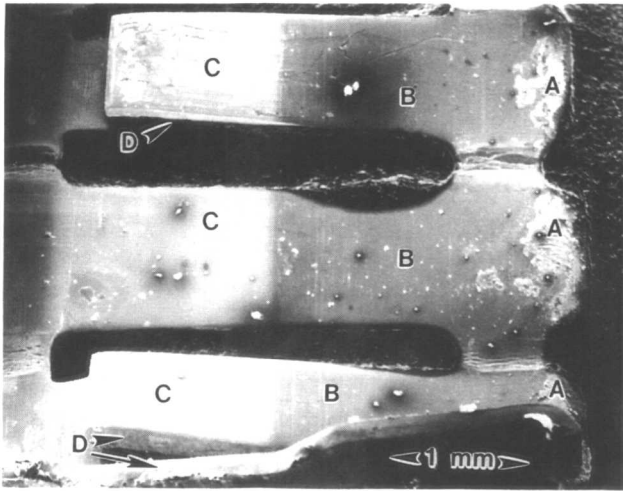


FIG. 5—A photo of an unfolded view of a typical contact used on the circuit boards.

### Discussion

There are several reasons for the excellent survivability of the complete system to the harsh environmental tests to which it was subjected. These include the housing, system materials, a limited number of separable connections, and connection design.

From the visual and AES results, it is obvious that the telephone housing acts as an excellent shroud. This occurs for two reasons. The low air-exchange rate caused by limited openings is the primary reason. The second reason is the potential sacrificial nature of the carbon steel from which the housing is made. This surface can adsorb and react with most pollutants as they enter the housing, thereby lowering the concentration before the pollutants can reach the electronic components.

The two primary exposed electronic system materials, tin and plastic, are both relatively inert to the types of pollutants used in the tests. The AES results shown in Fig. 2 for Sn verify that Sn does not readily continue to corrode after the first few nanometers of oxide have formed on the surface.

Gold-plated surfaces were only exposed to the atmosphere in two places on the circuit boards. The unshrouded, exposed, plated Au DIP lead frame was very corroded because of galvanic corrosion of the underlying Cu substrate at pores in the Au plating. However, this package was soldered into the circuit board, and the Au surface did not participate in the electrical performance of the circuit. The second Au surface was in the connector and is discussed below.

The copper alloy substrate in the connectors becomes exposed after the stamping and forming operation when the contact is manufactured. If this copper was exposed to the street atmosphere, a significant corrosion problem could exist. However, the shrouding effect of the assembled contact limits the amount of pollutant reaching the contact area, and the reactive nature of the copper tends to trap the diffusing pollutant at the entrance to the contact well. These two effects reduce the impact of pollutants in the actual contact region, as is shown by the following model. Consider a three-dimensional channel closed at one end and whose dimensions are  $x$  depth,  $y$  width, and  $z$  height, as illustrated in Fig. 6. Assume that the  $x$ - $y$  plane surfaces are made of copper and that  $y_0 \ll z_0$ . Then for the copper surface to corrode

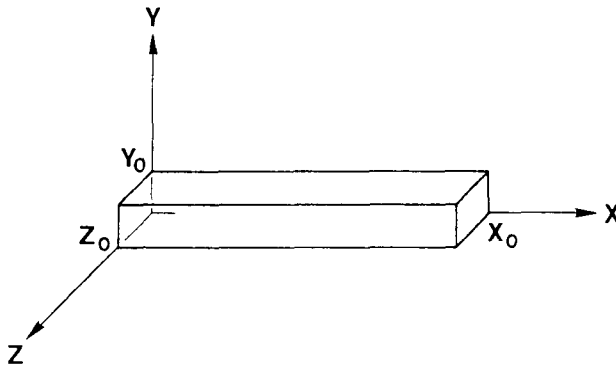


FIG. 6—Schematic illustration of a corrosion channel:  $Y_0 \ll Z_0$ .

down the length of the channel, the pollutant gas must diffuse past the copper at the open end of the channel. The time for the corrosion to proceed down the channel and accumulate on the walls to a thickness of  $M$  g/cm<sup>2</sup> is approximated by<sup>5</sup>

$$t = \left( \frac{2M}{DC_0} \right) \frac{X^2}{z} \quad (1)$$

Let  $D$ , the diffusion constant, equal  $0.2$  cm<sup>2</sup>/s; let  $C_0$ , the free air concentration of Cl<sub>2</sub>, equal  $20$  ppb, which equals  $5.6 \times 10^{-11}$  g/cm<sup>3</sup>; and let  $M$ , the mass density of the corrosion film, equal  $10^{-4}$  g/cm<sup>2</sup>. For the connector channel in this case, the approximate active depth is  $0.47$  cm and the approximate spacing between the pin and connector body (the channel in the example) is  $0.019$  cm. Thus the time needed to corrode the copper at the bottom of the channel to a  $1\text{-}\mu\text{m}$  depth is  $2.1 \times 10^8$  s or more than six years. Therefore, for the seven-day experiment described above, we only expect corrosion at the entrance to the channel and that is precisely what is observed. In the actual field case an equipment lifetime of much more than six years is needed, but the Cl<sub>2</sub> concentration in the outdoor air is much less than  $20$  ppb (and still less inside of the housing). Therefore, based on the assumption that our test atmosphere reflects a substantially accelerated street atmosphere corrosiveness, we expect the apparatus to last substantially longer than six years.

## Conclusions

We have demonstrated that an electronic coin telephone will operate normally after a seven-day exposure in a Battelle Class III atmosphere followed by exposure in a 95% RH atmosphere used for the electronic testing. In general, corrosion film thicknesses on Au plated or Cu circuit component surfaces were less than corrosion film thicknesses on control coupons. This is attributed to the circuit pack geometry and component shrouding. Specifically, we demonstrate that with reactive surfaces in a narrow channel, the corrosion film does not progress rapidly down the length of the channel. On Sn or nonmetallic surfaces, no significant corrosion was found as determined by AES and Ar<sup>+</sup> ion depth profiling.

<sup>5</sup> This derivation by R. Schubert and H. G. Tompkins (Motorola) will be published separately.

*Acknowledgment*

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**References**

- [1] Abbott, W. H., "Effects of Industrial Air Pollutants on Electrical Contact Material," *IEEE Transactions on Parts, Hybrids, and Packaging*, PHP-10, Vol. 24, 1974.
- [2] Rice, D. W., Suits, J. C., and Lewis, S. J., "Magnetic, Corrosion, and Surface Properties of Ni-Fe-Cr Thin Films," *Journal of Applied Physics*, Vol. 47, No. 3, March 1976, p. 1158.
- [3] Rice, D. W., Peterson, P., Rigby, E. B., Phipps, P. B. P., Cappell, R. J., and Tremoureaux, R., "Atmospheric Corrosion of Copper and Silver," *Journal of the Electrochemical Society*, Vol. 128, 1981, p. 275.
- [4] International Electrotechnical Commission 68-2-11, Test Ka, 3rd ed., 1981, Geneva, Switzerland.
- [5] International Electrotechnical Commission 68-2-42, Test Kc, 2nd ed., 1982, Geneva, Switzerland.
- [6] International Electrotechnical Commission 68-2-30, Test Db, 2nd ed., 1980, Geneva, Switzerland.
- [7] Abbott, W. H., "The Development and Performance Characteristics of Mixed Flowing Gas Test Environment," *IEEE Transactions on Components, Hybrids, and Manufacturing Technology*, CHMT-11, Vol. 11, No. 1, 1988, p. 22.
- [8] "Generic Physical Design Requirements for Telecommunications Products and Equipment," Bellcore Technical Reference: TR-TSY-000078, Issue 2, Bellcore, Piscataway, NJ, December 1988.
- [9] "Component Packaging and Interconnecting with Emphasis on Surface Mounting," ANSI/IPC-SM-780, Institute for Interconnecting and Packaging Electronic Circuits, New York, March 1988.
- [10] "Functional Product Class Criteria—Telephones," Bell System Voice Communications Technical Reference Publication 48005, American Telephone and Telegraph Company, 1980.

Edward S. Sproles, Jr.<sup>1</sup>

## Electrical Resistance of Wires Used as a Corrosion Rate Monitor

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**REFERENCE:** Sproles, E. S., Jr., "Electrical Resistance of Wires Used as a Corrosion Rate Monitor," *Corrosion of Electronic and Magnetic Materials, ASTM STP 1148*, P. J. Peterson, Ed., American Society for Testing and Materials, Philadelphia, 1992, pp. 11-20.

**ABSTRACT:** As a wire corrodes, its electrical resistance increases due to a loss of metallic cross-sectional area. By continuously monitoring resistance, corrosion can be monitored in the ambient where the wire is exposed. Although simple in principle, this technique has a number of practical problems when applied to atmospheric corrosion tests used with electronic equipment. These problems include: (1) the need to use very small diameter wires which are quite fragile; (2) the need to clean the wire in a reproducible and effective initialization process; and (3) the need to hold the wire in a resistance-measuring fixture without using solder and solder flux. This paper describes methods developed to overcome these problems and to implement the technique in a practical way for use as corrosion rate monitors for mixed gas atmospheric corrosion tests. Data are shown to illustrate the use of the method and to show the degree of reproducibility obtained between separate monitoring wires. The application of the method to fundamental studies of the effect of shielding on atmospheric corrosion is also illustrated.

**KEY WORDS:** copper, atmospheric corrosion, annealing, heat treatment

Laboratory atmospheric corrosion tests for electronic components require careful calibration and monitoring to obtain reproducible and meaningful test results on the components under test [1-3]. Ideally, a calibration and monitoring technique should be simple, accurate, and continuous to provide useful information promptly and efficiently. Change in resistance of metallic conductors has been used where the conductors are copper paths on printed circuit boards [4]. Such monitors are relatively easy to handle, but are readily available only with copper as the monitor material and require fabrication of appropriate test patterns on the test boards. Wires, however, are available in a wide range of materials and sizes. Wire is made in a continuous process; therefore, variations within the short lengths of wire required should be minimal.

In contrast, circuit boards are made in a batch process which may make them more susceptible to unit-to-unit variations. Furthermore, wires can be freely exposed to the ambient, while only one side of the sheet copper laminated to printed wiring boards can be exposed to the ambient; therefore, wires may show greater sensitivity to the ambient.

Wires have some obvious drawbacks as monitors. Fine wires are somewhat difficult to handle without breakage throughout the preparation and installation process; therefore, a robust fixture must be developed if the technique is to be practical for routine measurements. Connections to fine wires are also not easy. The fragility of the wire limits the options for screw terminations or other types of mechanical connections to the wire. Soldering is undesirable because it could: (1) introduce contamination from flux; (2) dissolve enough copper to reduce the wire cross section in the termination area; (3) set up an undesirable electrochemical couple.

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As a result, for the method to be practical, the user must develop fixtures and techniques to connect the measurement wires to the resistance measurement instrumentation, preferably without solder and solder flux.

This paper discusses results of exploratory studies using wires as corrosion rate monitors and explains methods developed to overcome some of the problems in their application to this technique.

### Development of Fixtures and Technique

One fixture to be developed is a measurement fixture in which wire can be exposed continuously to the test ambient while the resistance is monitored. Figure 1 shows the basic fixture developed to hold, expose, and monitor four wires. Each wire is freely exposed over the center portion of its length, approximately 50 mm. At each end of the wire, a cover presses the monitor wire against two measuring, or sensing, leads. These leads, made of gold wire, provided the four-wire connection to the monitor wire for precision resistance measurements. Silicone rubber pads backed up by a rigid plastic cover attached by screws provide the pressure.

Another fixture developed is the cleaning fixture. This fixture is made entirely of polymethylmethacrylate (PMMA) plastic and nylon screws. The fixture holds wires at the correct spacings to be later transferred to the measurement fixture with a minimum of disturbance and freely exposes the portion of the wire which will later be placed in the measurement fixture. The test wire is threaded onto the fixture and immersed in a series of liquid baths to bring the wire to an initial state of cleanliness. Figure 2 illustrates a cleaning fixture with wire installed in preparation for cleaning and transfer to the measurement fixture. Appropriate mechanical fixtures are provided so that the cleaning fixture and the measurement fixture can be fastened together without damage to wire already in place in the cleaning fixture. Figure 3 illustrates how the two fixtures are positioned in preparation for transfer of wire from the cleaning to the measurement fixture.

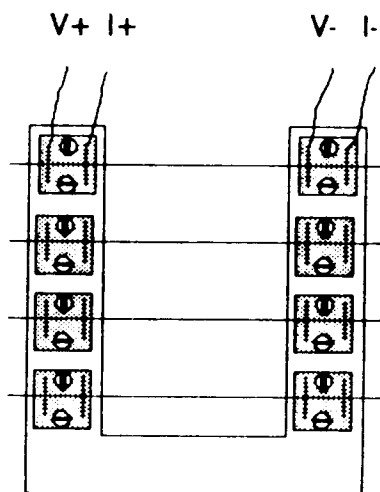


FIG. 1—Wire-holding and measurement fixture.