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MB20B BASE STOCK AS TARNISH PROMOTER OR PREVENTOR. (U)
APR 81 E G SHAFRIN, R J COLTON
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20. ABSTRACT (Continued)

Matched pairs (MB20B-coated versus bare) of model electroplated Au/Ag/Cu and Au/Cu coupons were exposed to various atmospheres (ambient, H₂S, H₂O) and temperatures. Although the MB20B film provided corrosion protection initially, it subsequently promoted a visibly more aggressive attack than on the uncoated surface. Visual evidence was supported by surface compositional data obtained by Auger spectroscopy and other analytical techniques. Thus, in addition to the C, Ag, and S present as the main tarnish ingredients on bare, gold-plated coupons, tarnish on the MB20B-coated coupon also contained Cu, Cl, and O. The latter, more complex constituency resembled that on discolored areas of operational, MB20B-lubricated slip-rings. To develop comparable constituencies on model coupons in the absence of MB20B, it was necessary to use highly aggressive atmospheres.

✓ Silver-to-antimony ratios were established as valid monitors of tarnishing and were used to confirm surface migration rather than mass transfer through the gold coating as the principal source of silver in the tarnish.

CONTENTS

SUMMARY iv

I. INTRODUCTION 1

II. EXPERIMENTAL APPROACH 1

III. RESULTS ON Au/Ag/Cu REFERENCE COUPONS
WITH MB20B 2

 A. Optical Evaluation 2

 B. Surface Composition of Discoloration on Gold 4

 C. Composition of Tarnish within Laboratory-Induced Scars .. 6

 D. Silver-to-Antimony Ratio as Monitor of the
 Tarnishing Process 7

IV. ANALYSIS OF Au/Ag/Cu FEMALE PCB CONNECTORS
WITH MIL-L-81846 8

V. EXPERIMENTAL RESULTS ON Au/Cu REFERENCE
MODELS WITH MB20B 9

 A. Optical Evaluation 9

 B. Surface Composition 11

VI. ANALYSIS OF DISCOLORED SLIP-RING 11

VII. DISCUSSION 12

VIII. ACKNOWLEDGMENTS 13

REFERENCES 30

A

SUMMARY

Electrical noise occurs in association with visible staining of gold surfaces in slip-ring assemblies lubricated with MB20B base stock (a combination of unprotected polyol esters). To determine whether the MB20B is implicated in stain formation attempts were made to duplicate the staining under laboratory-controlled conditions with and without lubricant present. Tarnishing was monitored visually for matched pairs (bare versus MB20B-coated) of model electroplated gold surfaces exposed to various atmospheres (ambient, H₂S, etc.), temperatures, and relative humidities. Surface analyses were performed by Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and X-ray emission energy dispersive analysis (XES-EDA). The compositional data were then used for assessing the role of the MB20B and for comparing the corrosion products with those from a real-life, MB20B-lubricated slip-ring.

At best, MB20B provides short-term corrosion protection (~1 month for ambient atmosphere and temperature). Over the longer term, not only does tarnishing occur, but the MB20B promotes a more generalized spatial distribution and heterogeneous chemical composition of the corrosion products than occur on MB20B-free counterparts. For MB20B-lubricated Au/Ag/Cu model systems there is less localization of the tarnish to areas adjacent to flaws in the gold coating. Silver-to-antimony ratios (established here as valid monitors of tarnishing) were used to confirm surface migration rather than mass transfer through the gold as the principal source of silver in the tarnish. The lubricant presence leads to additional elements (e.g., Cu, Cl, and O) and a more varied chemical environment within the tarnish layer along with the C, Ag and S present (as the main tarnish constituents) on bare gold-plate as well. This augmented constituency resembles that produced on bare Au/Ag/Cu only after contact with aggressive atmospheres. Similar compositions, but with enhanced copper and oxygen, characterized the discoloration on an actual slip-ring component; an additional, unexpected constituent was Mo. The extent to which these compositional variations and the locally varying thickness of the superficial tarnish layer affect electrical conductivity was not addressed.

As a thin film the unprotected MB20B (i.e., base stock) developed non-wetting behavior during the first few weeks exposure to the ambient atmosphere at 120°F; upon extended exposure, further degradation of the oil led to the presence of small patches of insulating solids. Neither development is desirable from lubrication or electrical conductivity standpoints.

In conclusion, no evidence was obtained to indicate that thin-film lubrication with MB20B base stock provides more than temporary corrosion protection. Over longer periods the MB20B promotes a more aggressive attack of the substrate. Electrical difficulties due to tarnish products may be further compounded by the presence of solidified organic degradation products. Incorporating anti-tarnish and anti-oxidation agents into the MB20B base stock may provide long-term corrosion protection.

MB20B BASE STOCK AS TARNISH PROMOTER OR PREVENTOR

I. Introduction

In slip-ring assemblies lubricated with MB20B base stock (1) undesirable electrical noise often develops in association with visible staining of gold surfaces of individual circuits. The extent to which the lubricant may be implicated in this stain formation is of concern. The staining of the slip-rings resembles that previously observed for unlubricated printed circuit board (PCB) female connectors of gold/silver/copper composition (2-5) where tarnish growth occurs at imperfections in the outermost gold coating. If a similar phenomenon is responsible for the staining of slip-rings, the MB20B could be contributing either constructively by limiting access of corrosive components of the atmosphere or adversely by facilitating tarnish development and/or migration.

The use of surface-sensitive analytical techniques to examine corrosion occurring under varying conditions in the presence of MB20B was proposed (6) as a method of investigating the problem. Comparison of the results with similarly treated specimens in the absence of MB20B was expected to provide guidance as to the desirability of retaining or eliminating MB20B as the lubricant. The similarity of slip-ring staining to corrosion of PCB connectors dictated inclusion of the latter in the present MB20B study.

II. Experimental Approach

This report summarizes the results of visual assessment and surface analysis by Auger electron spectroscopy (AES) of matched pairs of bare and MB20B-coated gold-plated specimens exposed to different sulfiding environments. As indicated in Table I, the specimens comprised laboratory-prepared reference models (both Au/Ag/Cu and Au/Cu) in the convenient geometric form of flat coupons and commercial bellows-form Au/Ag/Cu female PCB connectors representative of industrial production.

The sulfiding conditions are detailed in Table I; the reasons for their choice are indicated below. To ensure that both the tarnish attack of the metal surfaces and the degradation of the unprotected esters of the MB20B base stock simulate as closely as possible the conditions experienced by actual slip-rings, long-term exposures to the ambient were used. These involved prolonged exposure to mild tarnishing environments, i.e., laboratory air with its airborne sulfur-containing contaminants in conjunction with other types of contaminants, at temperatures (70°F and 120°F) and relative humidities comparable to those of slip-ring storage or operation. Alternatively, aggressive sulfiding conditions were employed to accelerate tarnishing; for these, higher temperatures (140°F) and relative humidities were used, together with specific sulfiding agents whose concentrations were enhanced chemically

relative to the remaining constituents of the atmosphere (7). To compensate for the more hostile conditions, the MB20B base stock was replaced by its formulated oil (MIL-L-81846) which contains an additive package designed to protect the oil from degradation when in contact with steels (1). These accelerated-tarnish specimens had been generated as part of a broader evaluation of various organic coatings for corrosion prevention of gold-plated connectors (7). The apparent similarity of slip-ring staining to corrosion on PCB connectors makes analytical results on the latter pertinent to the present investigation.

The AES analyses were performed using a Physical Electronics Industries Model 545 Scanning Auger Microprobe with a 5 μm diameter beam and an accelerating voltage of 5 keV. The AES results are presented here in terms of normalized Auger intensities (4). To a first approximation these can be considered equivalent to atomic percentages inasmuch as the data have been normalized to a total atomic constituency of one hundred. For cases where the surface carbon content varies widely, intercomparisons are facilitated by neglecting the carbon contribution. This is accomplished by normalizing the Auger intensities of elements other than carbon to a sum of the non-carbon constituency equal to one hundred. The designation "nc%" is used to indicate composition percentages based on non-carbon constituency.

Depth profiling was accomplished with a 2 keV Ar^+ ion gun at an ion current density measured at 25 $\mu\text{A}/\text{cm}^2$ using a Faraday cup. Although a sputter-removal rate for heterogeneous tarnish would be difficult to establish, a "rule of thumb" of 1-2 \AA removed per 1 $\mu\text{A}\text{-min}/\text{cm}^2$ ion dose is consistent with tarnish thickness estimates based on comparative heights of high- and low-energy gold Auger signals.

The scanning electron micrographs (SEM) were obtained with an AMR Scanning Electron Microscope, Model 1000, and the corresponding X-ray emission spectroscopic energy dispersive analyses (XES-EDA) by its associated Kevex-Ray 5100 X-Ray Energy Spectrometer.

III. Results on Gold/Silver/Copper Reference Coupons

A. Optical Evaluation

Au/Ag/Cu reference coupons were prepared at NRL to meet the thickness specified for platings on commercial PCB female connectors. An outermost gold plating (~0.6 microns) was deposited from a KCN Type, 24 KT gold bath onto a silver plating (~25 microns) deposited from a commercial high-speed silver-plating formulation onto a KCN-Ag strike. Two coupons were freshly cleaned (Reference 8) and then scored through their gold coatings to reveal a swath of the underlying silver approximately 3-4 mm long and 0.1-0.2 mm wide. After one of the pair had been lightly coated with MB20B base stock, each coupon was placed in its individual container, exposed to laboratory air but protected from dust. Periodically, the coupons were removed from their

respective containers and examined optically at magnifications from 1X to 70X for evidence of discoloration within the deliberate scratch or on the adjacent gold coating.

Long-term observations on both the bare and MB20B-coated specimens are recorded (to the nearest week) in Table II. Additional details are given below for observations on the uncoated coupon because they show (a) how closely the tarnish growth on the uncoated coupon matches literature descriptions of tarnishing (9,10), and (b) how different the tarnish appears from that developed in the presence of MB20B. The first week of exposure to the ambient produced no discoloration on the gold areas of either coupon, but tarnish was already visible within the MB20B-free scratch. Within ten days "haloes" of discoloration formed on the gold area of the uncoated coupon, parallel to and extending from the long sides of the deliberate scratch as well as from topographic features of the gold exhibiting no exposed underlying material even at 70X magnification. With continued exposure the width of the halo (from the near edge of the scratch to the outer edge of the discoloration) increased; as shown by the semi-log plot of halo width against exposure time (Fig. 1), the increase was approximately exponential during the first four months. In contrast, the discoloration on the coated coupon, although delayed in onset, was far more generalized and did not lend itself to quantification.

An indication of the differences in extent and localization of tarnish growth for the matched coupons is evident in the color photograph (Fig. 2) taken after the first four months' exposure. As exposure to the ambient continued, the outer edge of the longitudinal halo on the uncoated coupon became too poorly defined to permit continued diameter measurements. A second layer of discoloration appeared to well up, however, as an overgrowth spreading from the edge of the scratch over the initial tarnish growth. Similar overgrowths have been documented in the literature (9).

Visual evaluations indicate that, at room temperatures and humidities, the MB20B base stock (which has neither additives to protect the oil from degradation nor the substrate metal from attack) does provide short-term protection of the order of a month or so. Over longer periods, it is less effective, and, indeed, appears to contribute to a more generalized attack of the surface. This suggests that the initial protection was the result of a mechanical hindering (by the liquid film as a barrier) of access of sulfur-bearing materials and moisture to the substrate. Over the longer term, however, the nondependence of discoloration growth on the presence of exposed substrate metal suggests that a different process is occurring. One possibility is that, with aging, the esters comprising the MB20B hydrolyze and the degradation products promote attack (but not necessarily a sulfide attack) of the surface through the gold plating imperfections.

These results correlate with the observations of Kinzig and Murday (7) on female connectors where MIL-L-81846 and a

number of other candidates "afforded a modest amount" of tarnish protection in a $(\text{NH}_4)_2\text{S}$ atmosphere for shorter exposure, "but with longer exposure to sulfide, they became worse than the unlubricated control".

B. Surface Composition of Discoloration on the Gold

The surface analysis addressed two questions:

(1) Do the successive waves of tarnish on the uncoated metal indicate more than one mechanism of tarnish growth or migration to be operative? If so, the short-term protection afforded by MB20B might be attributed to its ability to suppress only one of the mechanisms.

(2) Do the patterns of localized versus generalized tarnish growth (corresponding to bare versus MB20B-coated specimens) reflect differences in surface elemental or chemical composition which can illuminate the MB20B role in tarnish promotion or suppression?

Table III presents the Auger analytical results for the discoloration on the gold surface of the bare specimen (unspattered) at the indicated distance from the edge of the deliberate scratch. Also included are data for one site within and one site at the edge of the scratch to show how readily the discoloration can be distinguished from the scratch. Because the sampling depth of Auger is so shallow ($\sim 5\text{-}30\text{\AA}$), analysis of sites closest to the scratch (i.e., 0.05 and 0.3 mm) is assumed to correspond to the second, more recent wave of tarnish, whereas that at 0.4 mm corresponds to the first wave. At the distance of 0.9 mm and greater, the tarnish is best characterized as diffuse, without necessarily being associated with localized growth.

Aside from carbon, the major constituents of the discoloration on the gold are Ag and S, with some O apparently associated, in part, with the occasional, obviously adventitious presence of alkali (Na and K). Completely absent from tarnish outside the scratch are copper and antimony.

With the notable exception of chlorine in the second wave, there is nothing in either the elemental constitution or concentration to differentiate the second wave from the other tarnish. Nor do the lineshapes of the sulfur low-energy Auger signals differ between the first and second waves, although considerable variation can occur elsewhere over gold coatings (cf. Fig. 3 and the sulfur columns of Tables III and IV).*

*Auger sulfur lineshapes can be used to distinguish various surface compositions (e.g., see Ref. 11). Each of the Auger lineshapes in Fig. 3 however occurs nondiscriminately for "pure" reagent grade chemicals and mineral samples of Ag_2S , Cu_2S , and CuS . This ambiguity requires further investigation.

The absence of AES evidence for Cu on the naturally tarnished specimen is in contrast to the detection of copper by X-ray photoelectron spectroscopy (XPS) on a reference coupon from the same sample lot immediately after a 2-hour exposure to the atmosphere above an aqueous $(\text{NH}_4)_2\text{S}$ solution (1977, unpublished data). Also detected on this accelerated-tarnish specimen were Au, Ag, S, and O. Subsequent to the XPS analysis, the accelerated-tarnish specimen had been isolated from direct contact with the ambient by storage within a gelatin capsule of limited (~ 2 cc) volume. After 3 years' storage, examination by Auger revealed a moderate carbon constituency (indicative of the effectiveness of the protective storage) and, along with the copper, the elements Au, Ag, S, and O found previously by XPS. The only additional element present was Cl, but at a concentration level so low (as indicated by AES) that its XPS signal could well have been obscured by background noise during the initial XPS examination. Absent from the tarnish is any evidence of antimony.

Comparison of the naturally tarnished, uncoated-specimen data (Table III) with that of its MB20B-coated counterpart (Table IV) reveals that: (i) a heavy carbonaceous film characterizes the coated specimen despite extensive solvent rinsing (with methanol and with acetone); and (ii) areas within scratches, although deficient in carbon relative to the intact surfaces of the uncoated specimen, show carbon enhancement relative to neighboring surfaces of the MB20B-coated specimen.

If the carbon constituency is disregarded, the major constituents of discoloration on both bare and MB20B-coated specimens are identical: silver and sulfur, in about the same atomic ratio (Ag:S-1.8:1 for both specimens). Differences occur in the lineshape of the low-energy sulfur signal and in the presence of oxygen; two items that are related. Lineshape "c" was consistently absent from the MB20B-coated surface, and oxygen was found at every site analyzed. This correlates with the general observation that oxygen is usually absent from those sites for which a "c" lineshape characterizes the sulfur signal, whereas a small amount of oxygen is generally detected where the other sulfur lineshapes occur. In view of the heavy carbon content of the coated surface and the fact that MB20B comprises oxygen-containing esters, one likely source for the oxygen is in residual lubricant film not removed by solvent cleaning. However, the O presence in roughly the same proportions vis-a-vis sulfur as in the bare specimen subjected to accelerated tarnishing argues that the O is integral to the tarnish. The origin of the chlorine is less clear cut. No chloro-organics are known to comprise the MB20B base stock, yet chlorine is found at every site on the MB20B-coated specimen in amounts that vary monotonically with carbonaceous contamination. Finally, it should be noted that while copper is occasionally detected in the discoloration, antimony is again completely absent outside the deliberate scratch.

For both the bare and MB20B-coated specimens, only a brief sputtering (with an ion bombardment dose of $25 \mu\text{A}\cdot\text{min}/\text{cm}^2$, corresponding to removal of a few tens of Angstroms of material) is sufficient to reveal the underlying gold surface and to greatly diminish both the silver and sulfur signals. This Auger evidence for a thin discoloration layer and for surface localization of the tarnish products is corroborated by the X-ray dispersive spectrograms taken in conjunction with the scanning electron micrographs shown in Fig. 4. The micron sampling depth of the XES-EDA (which far exceeds the 5-30 Å Auger sampling capability) detected the gold-plated layer but not sulfur, silver, nor chlorine.

C. Composition of Tarnish within the Laboratory-Induced Scars

Although major interest centers on the discoloration on the gold as the presumed actual site of the electrical interference, analysis of the composition of the deliberately scored areas after they have been allowed to tarnish provides valuable insights to the origin and extent of the tarnish development.

Considerable variation exists in elemental composition between adjacent sites within a single, deliberate scratch. Nevertheless, certain features are common to all the sites; these are exemplified by the data for single sites included in Tables III and IV for each of the naturally tarnished specimens. Thus, just as was observed for the discolored areas on gold, there is a higher percentage of carbon within the scar on the MB20B-coated specimen (85%) than the uncoated specimen (35% of the total atomic constituency). Among the non-carbonaceous constituents of the scars, very little gold (from the surface coating) and no copper (from the substrate) were detected in either the bare- or coated-specimen scars. Two metals were found, however: silver, as anticipated, and unexpectedly, antimony, in amounts comparable to the silver.

The principal non-metals found within the tarnished scars were oxygen, sulfur, and chlorine, with the latter far more prevalent in the MB20B-coated specimen than the bare. Correlations were observed between the O and Sb content as well as between the S and Ag. Although the average Ag:S ratio in the coated specimen (2.5:1) was approximately twice that of the bare coupon (1.2:1), there was no evidence from the low-energy sulfur lineshapes ("b" in both cases) to indicate major chemical differences between the sulfur compounds present in the scars. An alternate explanation for the ratio differences is that a significant fraction of the surface silver in the MB20B-coated scar is in the form of the chloride.

It should be noted that despite the low Cl presence determined by Auger for the surface of the bare scar, the deeper sampling XES-EDA analysis of both the tarnished and a freshly made scar found measurable amounts of chlorine in the silver layer. However, no sulfur was detected, indicating localization

of the sulfide but not the chloride to the outermost surface.

D. Silver-to-Antimony Ratio as a Monitor of the Tarnishing Process

An earlier study (3) of a sulfided Au/Ag/Cu reference coupon from the same sample lot as the present study also had detected antimony. Its association with a micro-flaw in the gold coating suggested an origin within the subjacent coating rather than the gold. In the present study antimony has been found wherever the gold coating has been deliberately removed and the underlying silver subjected to prolonged exposure. Moreover, the atomic concentration of antimony after such exposure ranges from a major fraction to several times the atomic presence of silver. Inasmuch as antimony was never detected in the silver-rich tarnish on top of the gold coating, these observations suggest a preferential migration of the exposed silver during sulfiding with a consequent apparent enhancement of the antimony at the origin of the migration. If this is the case, the Ag:Sb atomic ratio might provide a convenient monitor of the tarnishing process and, in the present instance, of the relative effectiveness of the MB20B in suppressing or fostering tarnish formation.

To examine this thesis, the Ag:Sb ratios observed on both gold-over-silver-plated and silver-plated surfaces after various treatments are collected in Table V. The second column indicates the exposure history of the sample as a whole, while the fourth column details the immediate exposure history of the specific analytical sites.

The data of Table V are consistent, indicating a large ratio of Ag:Sb to be characteristic of freshly exposed or de-tarnished silver, with a progressive decrease in the ratio as exposure continues. Thus, even though a low Ag:Sb ratio had developed during the 8 months ambient exposure of scratches in both the bare (#1a) and MB20B-coated (#2a) specimens, scratches freshly made immediately adjacent (#1b and #2b, respectively) showed the characteristically high Ag:Sb ratio of a freshly exposed surface. On aging (#2c), the ratio gradually declined.

For the Ag:Sb ratio to be useful as a monitor of the preferential migration of silver under tarnishing conditions, the apparent enrichment of antimony (consequent on the silver depletion) should be confined to the surface. Evidence of such surface enrichment was provided by Auger analysis of the un-sputtered specimen (Table V). Evidence that a similar disproportionment did not extend through the depth of the silver layer was obtained by X-ray energy dispersive analysis of the two scars shown in Fig. 4. This deeper-sampling technique indicated essentially identical metallic compositions for both the aged (#1a) and fresh (#1b) scratches, with no antimony registering in either case. This is the expected result if the antimony is concentrated at the surface, since the X-ray

technique has a quoted sensitivity of around 1 atom percent of the bulk concentration and this figure is close to the antimony concentration in freshly detarnished silver as determined by Auger.

To the extent that the Ag:Sb ratio is a valid monitor of tarnish formation and migration, the excellent agreement of the ratios for the 8-months old scars on the bare and the MB20B-coated specimens argues that, over an extended period, at least, the MB20B did not contribute to reducing or promoting tarnish formation. Moreover, the large difference in ratios between an aged scratch and a fresh scratch in its immediate vicinity indicates that a major source of the silver involved in the tarnish was the exposed silver at the scratch rather than silver which had migrated through the gold overlayer.

Although antimony within the silver plating did not contribute to the discoloration problem, its unanticipated presence and surface enrichment at exposed areas provides an object lesson on the potential for harm or good of unsuspected constituents present in what are normally considered minor concentrations. It should be pointed out that, although the present specimens are laboratory-prepared reference models, they were prepared from plating solutions available commercially and advertised for their applicability to electronics technology. Thus, the silver plating reported here was prepared using a commercial formulation for a high speed, mirror bright silver bath for which the manufacturer claimed better tarnish resistance than for pure silver and a contact resistance the same as that for contacts plated with silver from a bath with no brightener present.

IV. Analysis of Au/Ag/Cu Female PCB Connectors with MIL-L-81846

It had been presumed initially that the discoloration on slip-ring circuits had an origin analogous to that on female connectors for printed circuit boards (PCB). Therefore, it was of interest to examine tarnish products on commercially prepared Au/Ag/Cu female connectors. Several suitable connectors were available from a recent MARDAN candidate lubricant study by Kinzig and Murday (7). The connectors had been treated with the formulated version of MB20B (MIL-L-81846) prior to exposure to various accelerated sulfiding environments. The inclusion of sulfur- and nitrogen-bearing additives in the formulated oil (cf. Table I, footnote) precludes direct comparisons of the surface compositions of the connectors (Table VI) with the reference coupons (Tables III and IV). Nevertheless, certain observations deserve mention.

Among the metals, copper constitutes an appreciable presence at the surface of both the long-term, ambient and the accelerated-tarnish connector surfaces. In the H₂S-exposed, lubricant-free female connector, the Cu is comparable in concentration to that of the bare reference coupon after it, too, had been exposed to

accelerated sulfiding conditions; Cu had been absent, however, when the bare reference coupon had been subjected to long-term, ambient exposure (Table III). In the presence of the formulated oil, sulfiding of the connector resulted in a pronounced enhancement of Cu with no obvious concomitant enhancement of any anionic species. No attempt was made (by ESCA-XPS) to distinguish metallic from ionic copper in the tarnish. Additional evidence for the dominance of the copper constituency in the accelerated-tarnish products on the lubricated connectors comes from depth-profile studies (Fig. 5). Once the carbon contamination has been essentially eliminated by a brief sputtering (~2 minutes at 25 $\mu\text{A}/\text{cm}^2$), the Cu concentration rose far more than did the Ag; also, the high Cu concentration persisted to considerable depth.

A second observation is the marked variation observed in silver surface concentration from one site to another on a connector that had been exposed to $(\text{NH}_4)_2\text{S}$ while, presumably, being protected from mechanical abrasion by the MIL-L-81846 (Table VI). Among the non-carbonaceous constituents, Cu and Au are lower in concentration at sites characterized by high silver and high sulfur. Indeed, except for organic contaminants, the elemental composition and sulfur lineshapes at high-silver sites, were very similar to those obtained on connectors given the same aggressive sulfiding treatment with no lubricant present. As in the case of tarnishing of reference model coupons, the lubricant does not provide significant corrosion protection of the commercial connectors.

V. Experimental Results on Au/Cu Reference Models with MB20B

A. Optical Evaluation

Gold-on-copper specimens proved much more resistant to discoloration than did the systems containing an intermediate silver layer. Thus, at room temperatures (~70°F) and relative humidities ($\leq 50\%$), a five month exposure of the bare specimen failed to develop any discoloration of the gold, even though the laboratory-induced scratch had tarnished over the complete length of the exposed copper substrate within the first week of exposure. In contrast, the scratch on the MB20B-coated specimen developed only spotty tarnish within the copper scratch during that first week, but did show some discoloration on the gold adjacent to the copper within the third month of exposure. By five months the first area had darkened perceptibly and had grown in width, but not in length. A second area of darkening had developed, however, at a second location alongside the scratch.

Approximately the same tarnishing and discoloration behavior was observed on a second pair of Au/Cu reference coupons exposed to the ambient atmosphere at the higher temperature of 120°F (comparable to operational temperatures in some electronic gear) and a relative humidity augmented by evaporating distilled water to a relative humidity of 15% at 120°F which

corresponds to the amount of water contained in the same volume at 55% and 70°F.

There was one significant difference in the case of the elevated temperature specimens, however. Although both the room-temperature and high-temperature MB20B-coated specimens were initially bright and shiny, a haze developed on the gold areas of the higher temperature specimen within the first six weeks; at 7X magnification the haze was resolved into many fine, round droplets. If lubrication is based on the presence of a continuous, thin film of lubricant, such a transition from wetting to non-wetting presents a problem; in the case of a lubricant-flooded system, however, non-wetting is of less concern. One cause of non-wetting behavior is the adsorption of a poorly wettable species at the solid surface (12,13). A possible source for such a contaminant is the thermally assisted hydrolysis of the unprotected polyol tetraester component of the MB20B base stock. One of its theoretical hydrolysis products, caproic acid, has demonstrated oleophobicity (i.e., poor wetting by organic liquids) (13). By the end of three months the transparent material was more viscid and amorphous in appearance. When, after 8 months exposure, the MB20B-coated specimen was solvent cleaned prior to insertion in the Auger microprobe vacuum system, some of these minute blobs resisted solvent removal. Subsequently, the strong charging and deflection of the electron beam whenever Auger analysis of these areas was attempted indicates the transparent material to be insulating and thus, a potential threat to the high electrical conductivity required in slip-ring operation. The blobs may represent residual polymerized lubricant base stock.

It should be pointed out that formulated MB20B (i.e., base stock with protective additives present) survives corrosion-oxidation tests (1) for 72 hours at 350°F in the presence of copper with only an 0.76 increase in neutralization number (i.e., a measure of oil stability expressed in milligrams of KOH required to neutralize one gram of oil), a 5% increase in viscosity at 100°F, and no insolubles or gum in the clear final sample. Under thin-film stability tests no lacquer, sludge or particulate matter was detected after 6 1/2 hours at 375°F.

In view of the significance of adsorbed water in the corrosion of copper surfaces (14), the room-temperature exposure specimens were transferred at the end of five months exposure from the ambient RH ($\leq 50\%$) to a chamber in which the RH could be increased to 75-85% without changing either the temperature or access to air-borne sulfide contamination. Even after three months under these more aggressive conditions, there was still no visible change on the gold surface of the uncoated Au/Cu reference specimen. The discoloration on the gold of the MB20B-coated specimen had continued to expand and intensify in color throughout this period, however.

Ambient exposure tests were terminated after a total of 8 months exposure in order to perform Auger surface analyses.

B. Surface Composition

Despite variations in treatment and discoloration behavior, all four Au/Cu coupons shared certain compositional features in common: their carbon constituency was higher within the deliberate scratch than on the gold (Table VII). Copper was present at every site sampled on the gold, although it represented a smaller percentage of the non-carbon constituency on the gold than it did within the scratched areas. The chlorine constituency correlated reasonably with the Cu, being considerably higher within or near the scratched area than further away on the gold. The sulfur concentration varied widely; higher S concentrations were frequently (but not exclusively) found at sites where there was Auger evidence for silver being present. It should be noted that, although a silver layer as such was not present in these reference specimens, gold plating often contains a small amount of silver (15). Lineshape "a" characterized all sulfur signals originating outside the scratched areas; within the scratches, "a" predominated, but "b" also occurred.

From the standpoint of the present investigation, the most significant features of surface composition were the wide variations in copper constituency and associated chlorine with no apparent correlation to visible discoloration and the presence of silver.

VI. Analysis of Discolored Slip-Ring

A segment of a gold slip-ring which had discolored during use had been analyzed previously at NRL (1979, unpublished). As expected for real-life components, there was considerable site-to-site variation in color and texture of the discoloration; AES showed a wide variation in surface composition as well (Table VIII), but with no correlation to the discoloration.

Although the ring resembled the MB20B-lubricated Au/Ag/Cu reference coupon in having appreciable carbon content (60-80%) it differed in other respects. All nine ring sites analyzed showed Mo, Cu and Na, but silver was not always present. The source of the molybdenum is not known; Mo was not reported to us as being a constituent of the slip-ring materials of construction or lubricant nor has Mo been identified in the AES spectra taken of brushes analyzed at the same time as the discolored ring segment.

Among non-metals, O was the most prominent, representing from one- to two-thirds of the non-carbon composition. Also present in appreciable percentages of the non-carbon constituency was N (10-20%). A possible N source is the cyanide bath from which the gold was electroplated. MB20B can be eliminated as a source because: (i) N is not present in the base stock polyol, and (ii) no N is detected by AES of the tarnish on MB20B-coated Au/Ag/Cu. The presence of N in tarnish on both bare and coated Au/Cu specimens, however, suggests a contaminant with an affinity

for copper. The S concentration varied widely; significantly, it was essentially absent from one highly discolored site despite the presence of both Cu and Mo. This argues against a molybdenum sulfide lubricant having been the source of Mo. The last non-metal of interest is chlorine. Because of the spectral overlap of Cl and Mo signals, detection and quantification of low concentrations of Cl is difficult. At no site on the ring was there any evidence of a large Cl presence in the discoloration.

VII. Discussion

The present study on the tarnishing of Au/Ag/Cu reference models corroborates observations in an earlier study of female PCB connectors (7) that, while MB20B may provide temporary protection against corrosion, over the longer term the corrosion is worse than on the unlubricated gold-plated surfaces. The MB20B appears to suppress the earliest tarnishing mechanisms, particularly those associated with the presence of exposed silver. When tarnishing does eventually occur, however, the corrosion is more widely distributed and more heterogeneous in composition with MB20B present than without.

Early success in preventing tarnishing could be due to the lubricant simply interposing a barrier preventing physical access of the atmosphere (or certain components thereof) to the exposed silver. Both the localization of the initial tarnish to the edges of exposed silver and the AES evidence of a shift in the Ag:Sb ratio at the very surface of the silver scar argue that the principal source of the early tarnish is the silver exposed at the scar. Since the major inorganic constituents of the early tarnish are Ag and S (the latter in a single chemical environment), to be effective the physical barrier would only need to prevent access of sulfur-bearing contaminant itself or of any other contaminant (such as moisture) which is necessary for the silver-sulfide reaction to occur (14).

Tarnish developing in the presence of MB20B not only shows lessened dependence on the exposure of Ag, but the appearance of Cu in the tarnish product. Additionally, there is a more varied elemental presence among the anions (i.e., Cl and O) as well as a more heterogeneous chemical environment of the S. Although these are features absent from tarnish found on bare Au/Ag/Cu systems exposed to mild tarnishing conditions, they are characteristic of corrosion products on bare systems after exposure to aggressive atmospheres. Moreover, because features characterizing tarnish on MB20B-coated reference models appear even more pronounced for actual slip-ring components, the MB20B base stock should be considered a tarnish promoter over a long period of time or under adverse conditions. The tendency of the lubricant to become non-wetting and to solidify when used in thin-film lubrication makes it even less desirable for slip-ring application.

Left unresolved is how adversely electrical conductivity is affected by a shift from an Ag,S- to a Cu,O-dominated surface

composition even though these represent only a fraction of an essentially carbonaceous contaminant layer.

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Table I: Experimental Materials and Conditions

Ident. No.	Metal Specimens ^a			Lubricant	Sulfiding Conditions			
	Composition	Form	History		Atmosphere	Temp. of	RH, %	Exposure Time
1	Au/Ag/Cu	Coupon	Lab-prep.	None	Ambient	70±5	<50	8 mos
2	" "	"	"	MR20R base stock ^b	"	"	"	"
3	" "	"	"	None	Over aq. (NH ₄) ₂ S sol'n	70	100	"
4	" "	Fem. Connectors	1979-Mfg., unused	MIL-L-81846C	Ambient	Uncontrolled		~6 mos
5	" "	"	"	"	4-55ppm H ₂ S over aq. (NH ₄) ₂ S	77	100	3x(12 hrs)
6	" "	"	"	None	"	"	"	"
7	" "	"	"	MIL-L-81846C	1000ppm H ₂ S	77 140	78 14 at 140°Fd	12 hrs
8	" "	"	Old, used	"	"	140	14 at 140°Fd	"
9	Au/Cu	Coupon	Lab-prep.	None	Ambient	70±5	<50	First 5 mos Next 3 mos
							100	

Table continued on next page.

Table I: Experimental Materials and Conditions - Cont'd.

Ident. No.	Metal Specimens ^a			Lubricant	Sulfiding Conditions			
	Composition	Form	History		Atmosphere	Temp °F	RH, %	Exposure Time
10	Au/Cu	Coupon	Lab-prep.	MB20B base stock	Ambient	70±5	<50 100	First 5 mos Next 3 mos
11	" "	"	"	None	Ambient, closed container	120±2	15 at 120°F	8 mos
12	" "	"	"	MB20B base stock	"	"	"	" "
13	Ag/Cu	"	"	None	"	Uncontrolled	"	3 yrs
14	" "	"	"	"	Freshly detarnished	70	<50	<1 hr

^aCleaned and detarnished according to Ref. (8), except for specimen #13 which was stored immediately after electro-plating.

^bBase stock: 65 w/o bis(2-ethylhexyl) azelate and 35 w/o pentaerythritol tetracaproate
^cMB20B finished with 1 w/o barium dinonylnaphthylene sulfonate (rust inhibitor), 1 w/o alkylated phenyl-alpha-naphthyl amine (antioxidant), & 0.2 w/o benzotriazole (metal deactivator).

^dCorresponding to 78% RH at 77°F.

^eCorresponding to 51% RH at 77°F.

TABLE II
VISUAL LOG OF PAIRED SPECIMENS (bare versus MB20B-Coated) EXPOSED TO AMBIENT SULFIDE CONTAMINATION

Specimen Exposure T RH	Au/Ag/Cu			Au/Cu								
	70°F 15-35%			70°F 15-35%			120°F 15% (at 120°F)					
Condition	Bare			+MB20B			Bare			+MB20B		
	Gold	Scratch	Condition	Gold	Scratch	Condition	Gold	Scratch	Condition	Gold	Scratch	Condition
0	Bright	Bright	Bright	Bright	Bright	Bright	Bright	Bright	Bright	Bright	Bright	Bright
1 wk	"	Tarnish	"	"	Wide-spread tarnish	"	"	Localized tarnish	"	Slight tarnish	"	"
2 wks	Halo*	"	"	"	"	"	"	"	"	"	"	Slight tarnish
3 wks	"	"	"	"	Tarnish	"	"	"	"	"	"	"
1 mo	"	"	"	"	General mottling	"	"	"	"	"	"	Tarnish
2 mos	"	"	"	"	"	"	"	"	"	"	"	"
3 mos	"	"	"	"	"	"	"	Faint halo	"	"	"	"
4 mos	"	"	"	"	"	"	"	"	"	"	"	"
5 mos	2nd halo over 1st	"	"	"	"	"	"	"	"	"	"	Changed
6 mos	"	"	"	"	"	"	"	"	"	"	"	Dis-colored

* Halo sufficiently well defined that measurements of its width could be made over several months

TABLE III
EFFECT OF EXPOSURE CONDITIONS ON SURFACE COMPOSITION OF UNLUBRICATED GOLD/SILVER/COPPER REFERENCE COUPONS

Specimen Identification		Auger Intensities Normalized to									
Exposure: Atmosphere Temperature Time	Distance from near edge of scratch (mm)	Σ Total Constitu- ency = 100	Metals			Σ Non-Carbon Constituency = 100			Non-Metals		
			Gold**	Copper	Silver	Anti- mony	Sodium	Potas- sium	Sulfur***	Chlorine	Oxygen
<u>Natural Tarnishing</u>											
Ambient 70°F 8 Months	In scratch* Edge of "	14 37 33 31 32 34 34 30 41 35	- - - - - - - - - -	- - - - - - - - - -	12 47 63 65 64 64 63 60 56 57	44 9 - - - - - - - -	- - - - - - - - - -	- - - - - - - - - -	- - - - - - - - - -	- - - - - - - - - -	31 5 - - - - - - 2 1 1 10 1
<u>Accelerated Tarnishing****</u>											
Over aqueous (NH ₄) ₂ S sol'n 70°F 2 Hours	Random site " " " " " " " "	58 42 44 42 36 34	2 24 3 12 29 65	12 6 8 3 5 3	47 43 47 47 40 22	- - - - - -	- ? ? 1 1 2	- - - - - -	- - - - - -	- - - - - -	2 1 6 2 2 3

* Data given are for single site within the scratch; although considerable site-to-site variation occurs, all sites within scratch have appreciable amounts of Sb and O.

** Normalized intensity for high-energy Au (MNN) Auger signal.

*** See Fig. 3 for corresponding lineshapes (a, b, or c) of low-energy S (KLL) Auger signal

**** Auger data taken after 3 years' storage of specimen in closed container; XPS examination immediately after sulfiding identified C, Au, Cu, Ag, S, and O as tarnish constituents.

TABLE IV
 SURFACE COMPOSITION OF MB20B-LUBRICATED GOLD/SILVER/COPPER REFERENCE COUPONS AFTER NATURAL TARNISHING

Specimen Identification		Auger Intensities Normalized to									
Exposure: Atmosphere Temperature Time	Distance from near edge of scratch (mm)	Σ Total Constitu- ency = 100 Carbon	Metals			Non-Metals					
			Gold	Copper	Silver	Anti- mony	Sodium	Sulfur**	Chlorine	Oxygen	
<u>Natural Tarnishing</u>											
Ambient	In scratch*	83	-	-	37	20	10	-	13 ^b	8	13
70°F	Edge of "	89	-	-	26	26	-	-	18 ^b	14	16
8 Months	< .1	79	-	-	59	-	-	-	37 ^b	4	-
	0.1-0.2	75	-	-	57	-	7	-	29 ^{a-b}	4	3
	~0.5	69	-	-	62	-	2	-	34 ^a	1	2
	~2	72	-	2	58	-	1	-	35 ^a	2	2
	~3	75	-	8	56	-	-	-	31 ^b	2	3

* Data given are for single site within the scratch; considerable site-to-site variation occurs, but all sites within scratch have appreciable amounts of antimony and oxygen.

** See Fig. 3 for corresponding line shapes of low-energy sulfur Auger signal.

TABLE V
SILVER-TO-ANTIMONY RATIOS OF ELECTROPLATED SPECIMENS AFTER VARIED EXPOSURES

Electroplating Profile	Specimen History	Exposure History of Analysis Site		Ag:Sb Ratio*		
		Identification	Site Description/History	Range of Ratios	Average of Ratio	(No. of Spots Analyzed)
Au/Ag/Cu	Bare metal; 8 mos. exposure to ambient**	1a	Deliberate scratch through Au; exposed 8 mos. to ambient	0.3-6.1	3.1	(5)
Au/Ag/Cu	Chromated; accelerated sulfiding***; 3 mos. storage, enclosed	1b	Fresh scratch, made subsequent to 8 mos. exposure	27-47	37	(8)
Au/Ag/Cu	MB20B-coated; 8 mos. exposure to ambient	2a	20-micron pinhole; exposure same as specimen as a whole	0.9	0.9	(1)
Au/Ag/Cu	Same, MB20B freshly removed before scratching	2b	Deliberate scratch through Au; exposed 8 mos. to ambient	1.0-1.8	1.5	(3)
Ag/Cu	Bare metal; stored 3 yrs., enclosed	2c	Fresh scratch, made subsequent to 8 mos. exposure	25-44	36	(3)
Ag/Cu	Above specimen, freshly detarnished****	13a	Scratch 2b after 7 wks. exposure to ambient	15.5-15.8	15.7	(2)
		13b	Lightly tarnished	9.2-15.5	12.0	(3)
		13c	Bright metal (physically protected)	13.4	13.4	(1)
			Freshly detarnished	40-96	61	(6)

* Atomic ratio derived from Auger intensities normalized by Phi Handbook sensitivity factors appropriate to beam voltages employed for specific site.

** Ambient refers to laboratory atmosphere at $70^{\circ} \pm 8^{\circ}\text{F}$ and $\text{RH} < 50\%$.

*** Accelerated sulfiding involved 2 hrs. exposure over 0.01% aqueous solution of $(\text{NH}_4)_2\text{S}$.

**** Detarnished with thiourea, oxalic acid solution.

TABLE VI
SURFACE COMPOSITION OF Al/Ag/Cu FEMALE CONNECTORS AFTER VARIFD EXPOSURES

Specimen History/Identification				Auger Intensities Normalized to										
Origin	Use	Lubri- cant	Exposure: Atmos. Ident. No.*	Σ Total Consti- tuency = 100 Carbon	Σ Non-Carbon Constituency = 100					Non-Metals				
					Copper	Silver	Anti- mony	Misc.	Sulfur**	Chlorine	Oxy- gen	Nitro- gen		
1979	New	MIL-L- 81846	Ambient, #4	83	-	33	0-4	-	-	15 ^a	4	21	26	
1979	New	"	H ₂ S, #7	63	-	56	6	-	-	11 ^a	1	5	20	
Old	Used	None	H ₂ S, #8	71	-	8	3	-	Na-11	9 ^{a-b}	6	63	-	
1979	New	MIL-L- 81846	(NH ₄) ₂ S, #5	55	10	6	27	-	Na-3	35 ^a	7	3	9	
			High-silver areas (2)	58	21	14	5	-	Na-9	25 ^a	3	10	14	
			Low-silver areas (3)											
1979	New	None	(NH ₄) ₂ S, #6	-	12	13	34	-	-	34 ^a	-	-	-	

* See Table I for exposure details

** See Figure 3 for corresponding lineshapes of low-energy sulfur Auger Signal

TABLE VII
SURFACE COMPOSITION OF GOLD/COPPER SPECIMENS EXPOSED TO AMBIENT AT 70°F, HIGH RH *

Identification		Auger Intensities Normalized to											
Coating	Site vis-a-vis scratch	Σ Total Constituency = 100 Carbon	Σ Non-Carbon Constituency = 100					Non-Metals					
			Metals			Calcium		Sulfur	Chlorine	Oxygen	Nitrogen		
			Gold	Copper	Silver	Sodium							
<u>Uncoated</u>													
	In scratch	73	16	56	-	-	-	-	2.4	7.8	8.6	9.4	
	" "	81	-	58	-	-	-	-	3.4	9.1	12	18	
	Close to "	64	64	14	2.2	-	-	10.5	0.8	3.6	4.6		
	Further from "	65	50	25	1.0	1	-	9.7	2.6	4.6	5.7		
	" "	67	64	14	2.7	-	-	7.5	1.3	6.1	4.2		
	" "	42	51	12	2.5	8	-	20	0.9	3.5	1.9		
<u>MB20B-Coated</u>													
	In scratch	81	-	65	-	-	-	4.5	12	16	3		
	" "	62	-	13	-	-	9	9.7	2	51	14		
	Near "	78	18	52	-	-	-	6.5	12	8	4		
	Further from "	66	43	28	?	-	-	15	2	4	8		
	" "	74	35	25	?	-	-	24	4	9	4		

* Total exposure = 8 months, of which first 5 were at RH < 50% and only the last three at 75-85%.

TABLE VIII
SURFACE COMPOSITION OF DISCOLORED GOLD SLIP-RING ASSEMBLY (LUBRICATED WITH MB20B-BASE STOCK)

Visual Appearance of Analysis Site	Auger Intensities Normalized to Σ Non-Carbon Constituency = 100										
	Σ Total Constituency = 100 Carbon	Metals					Non-Metals				
		Gold*	Copper	Silver	Molybde- num **	Sodium	Misc	Sulfur***	Chlorine**	Oxy-	Ni-
Gold Color	78	-	4	?	18	7	5 ^{b-c}	1.5	48	16	
Very Discolored	77	-	6	2	15	5	3 ^a	1.2	59	9	
"	75	?	22	4	7	7	21 ^{b-c}	0.7	25	13	
"	74	-	5	-	12	10	S1	2	59	11	
Discolored	71	-	13	?	11	4	18	2	33	18	
Gold & Discolored	70	-	7	5	7	8	Mg,Si 22 ^a	2	37	12	
Discolored	60	?	7	3	16	3	8	2	40	21	
"	60	-	3	1	18	2	3	3	62	8	
"	57	Au	17	2	11	7	30 ^a	0.4	23	10	

* Low-energy Au (KLL) Auger signal detected.

** The normalized intensity for Mo₂₂₁ was used to establish the Mo₁₈₆ contribution to the Auger signal from which the normalized intensity for Cl₁₈₁ was derived.

*** See Fig. 3 for corresponding lineshapes of low-energy S (KLL) Auger signal.

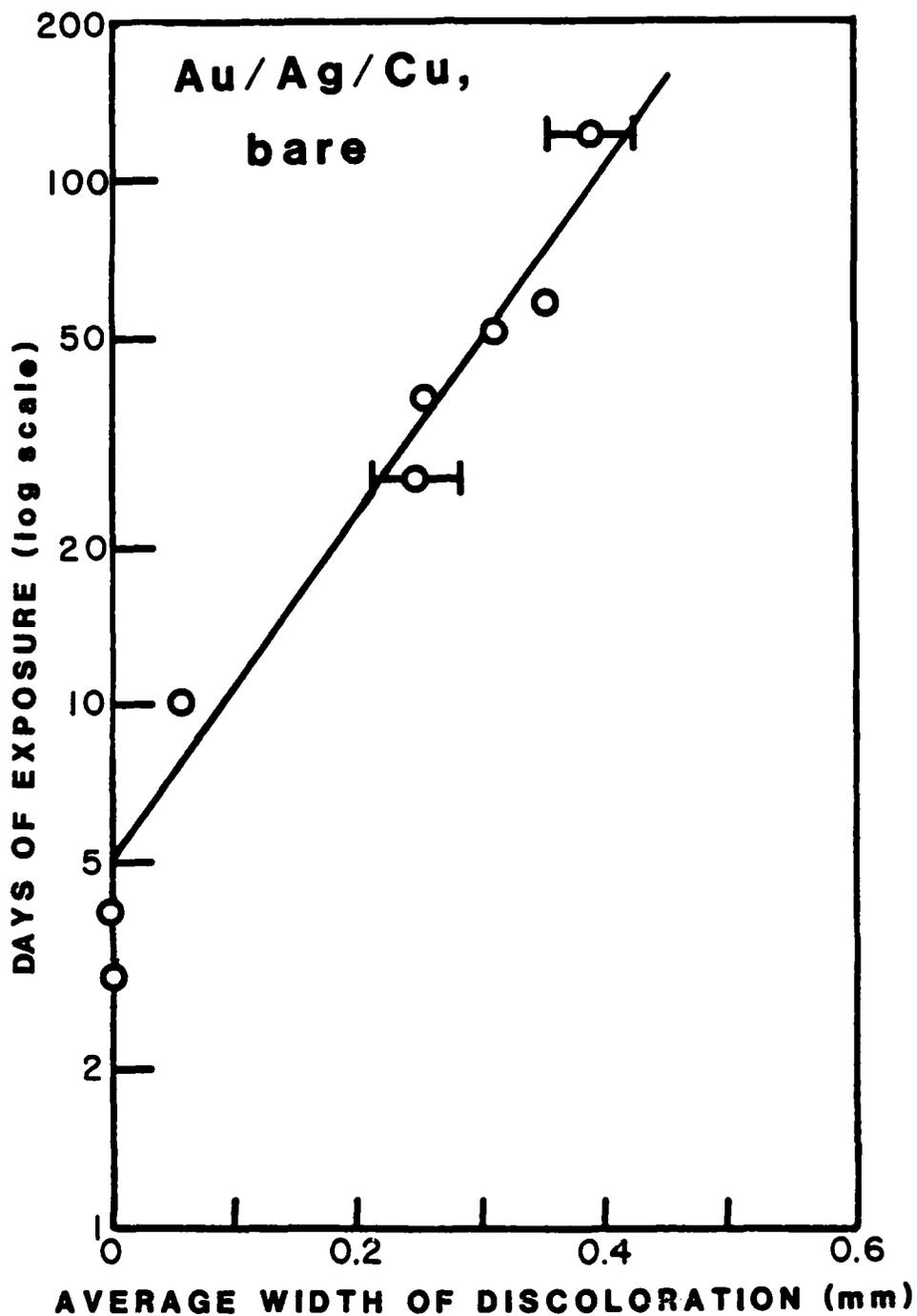


Fig. 1 — Semi-log plot of the rate of growth of the discoloration "halo" parallel to the long sides of a laboratory-induced scar through the gold coating of a bare Au/Ag/Cu reference coupon exposed to the ambient at room temperatures and humidities

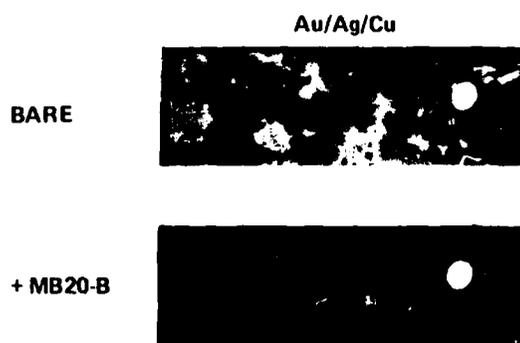


Fig. 2 — Color photograph showing the difference in the extent and pattern of discoloration between bare and MB20-B-coated reference coupons exposed to ambient for 4 months

SULFUR AUGER LINESHAPES

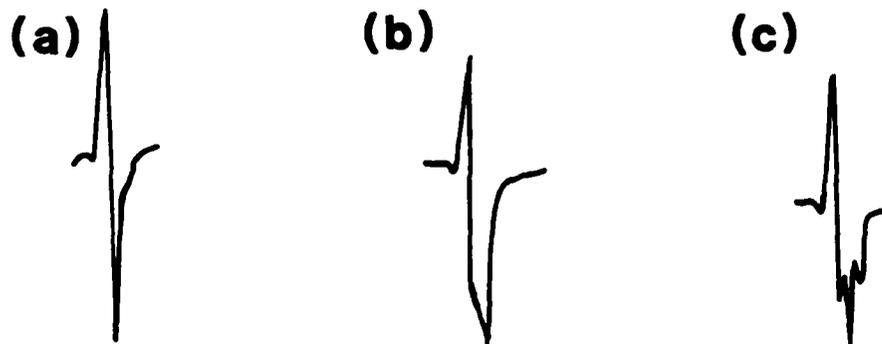


Fig. 3 — Comparison of the lineshapes for the low-energy sulfur Auger signals. The designations shown here are used to identify lineshapes in data tabulations of Tables III through VI.

GOLD/SILVER/COPPER COUPONS

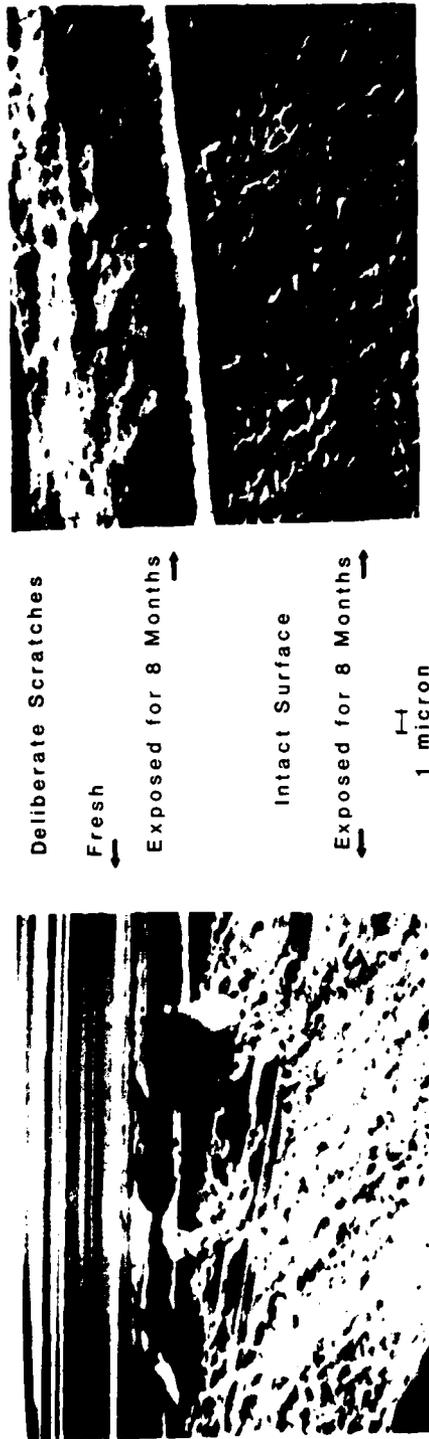
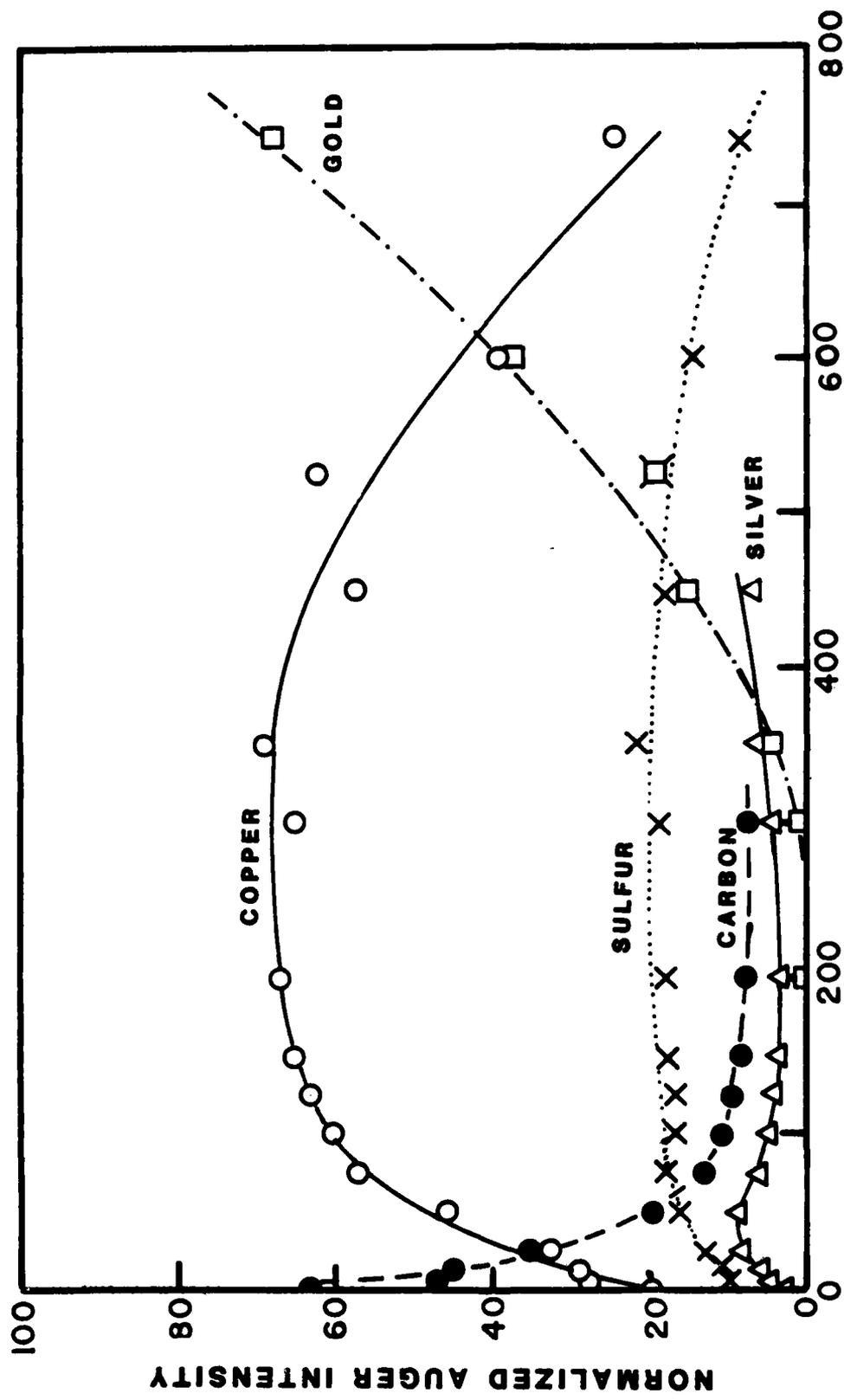


Fig. 4 — Scanning electron micrographs of a bare Au/Ag/Cu reference coupon after 8 months exposure to the ambient. Results of X-ray energy dispersive analyses on the intact gold coating and the aged and fresh scars are given in text; results of the corresponding Auger analyses are given in Table V for the aged scar (#1a) and the freshly made scar (#1b).



ION DOSAGE, microamp-min/cm²

Fig. 5 - Auger/sputter depth profile of a new Au/Ag/Cu female connector after exposure to H₂S with MIL-L-81846 present (#7 of Tables I and VI)

REFERENCES

1. C.H. Blachly, V.G. FitzSimmons, and H. Ravner, "NRL-MB-20B, An Improved Instrument Ball Bearing Lubricant", NRL Report 7087, 6 March 1970.
2. J.S. Murday, E.G. Shafrin, and R.C. Bowers, "Electronics Corrosion Report", NRL Letter Report 6170-844:JSM:blr, 22 Dec. 1977.
3. E.G. Shafrin, "Scanning Auger Microanalysis of MARDAN-Related Specimen", Memorandum 6170-139:EGS:fdt, 29 March 1978.
4. J.S. Murday and E.G. Shafrin, "Interim Report on Electronics Corrosion", NRL Letter Report 6170-684a:EGS:kvk, 20 December 1978.
5. E.G. Shafrin, J.S. Murday, J.D. Guttenplan, and L.N. Hashimoto, "Chromate Film Used for Chemical Corrosion Control on Gold-Plated PCB Connectors", Applications of Surface Science 4, 456-465 (1980).
6. Minutes, 6 June 1979 Meeting, SP-23, Crystal City, VA.
7. B.J. Kinzig and J.S. Murday, "Studies of Corrosion Prevention of MARDAN Connectors by Organic Coatings", NRL Memorandum Report 4230, 9 June 1980.
8. NAVORD OD 45723 ATI No. 0001A, Refurbishment Procedure for MARDAN Computer D9F-A, 9 June 1976.
9. W.H. Abbott, "Recent Studies of Tarnish Film Creep", 24th Holm Conf. on Electrical Contacts, 1978.
10. H.E. Bennett, R.L. Peck, D.K. Burge, and J.M. Bennett, "Formation and Growth of Tarnish on Evaporated Silver Films", J. Appl. Phys., 40, 3351 (1969).
11. N.H. Turner, J.S. Murday, and D.E. Ramaker, "Quantitative Determination of Surface Composition of Sulfur Bearing Anion Mixtures by Auger Electron Spectroscopy", Anal. Chem. 52, 84 (1980).
12. E.F. Hare and W.A. Zisman, "Autophobic Liquids and the Properties of Their Adsorbed Films", J. Phys. Chem. 59, 335 (1955).
13. H.W. Fox, E.F. Hare, and W.A. Zisman, "Wetting Properties of Organic Liquids on High Energy Surfaces", J. Phys. Chem. 59, 1097 (1955).

REFERENCES (CON'T)

14. S.P. Sharma, "Adsorption of Water on Copper and Cuprous Oxide",
J. Vac. Sci. Tech. 16, (5) 1557 (1979).
15. F.H. Reid and W. Goldie, "Gold Plating Technology",
Electrochemical Publications Limited, Ayr, Scotland, 1974.