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Sulfide Corrosion of Silver Contacts During Satellite Storage

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Delays in satellite launchings may require satellites to be stored on the ground for up to 6 years, and, in some instances, electrical "scratchy" noise on pure silver electrical connectors may develop in as little as 6 months. This problem has been attributed to the growth of silver sulfide, Ag_2S, a semiconductor, on the silver contact surfaces. We offer suggestions that could improve storage specifications for satellites where Ag_2S might be reduced to a level (thickness) where it does not pose a problem. This review of Ag_2S growth might also be applicable to other satellite components where Ag is present, e.g., mirrors.

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I. INTRODUCTION

Increasing delays are expected in satellite launchings, requiring satellites to be stored on the ground for possibly up to 6 years. In some instances, electrical "scratchy" noise on pure silver electrical connectors develops in as little as 6 months. This problem has been attributed to the growth of silver sulfide, Ag_2S, a semiconductor, on the silver contact surfaces. In reviewing the literature, we have set forth suggestions that could improve storage specifications for satellites where Ag_2S, although not entirely eliminated, might be reduced to a level (thickness) where it does not pose a problem. This review of Ag_2S growth might also be applicable to other satellite components where Ag is present, e.g., mirrors.

II. DISCUSSION

A. CORROSIVE FILM GROWTH ON SILVER

The sulfidation of silver depends primarily on two parameters: the amount of reduced sulfur gases present and the water vapor (humidity) at the silver surface.

Silver sulfide is the most common corrosive film formed indoors on silver; outdoors, corrosion films usually contain a mixture of silver chloride, silver sulfate, and silver sulfide.[1] Silver does not react with oxygen to form silver oxide at ambient conditions.[2] The major sulfur-containing compounds in the environment are listed in Table 1,[3] with H_2S and carbonyl sulfide (OCS) responsible for the most silver sulfidation. H_2S, sulfur dioxide (SO_2), and to a lesser extent carbon disulfide (CS_2), dominate the urban areas, but SO_2 and CS_2 sulfidation of silver is relatively slow or nonexistent.[4-7] OCS is the most abundant sulfur-containing compound in nonurban areas, having a nearly uniform concentration throughout the globe. Studies of the effects of various gases on the sulfidation of silver, performed in the laboratory, cannot exactly emulate the type of sulfidation found in the field. A multitude of chemical compounds can be formed in field environments, each with its specific hardness and conductivity. However, since satellites are stored in controlled indoor environments rather than in the field, papers that deal with laboratory rather than field results should be of greater significance.

TABLE 1. Concentration of Atmospheric Sulfur Gases (ppb)

Species	Urban, Industrial Areas	Remote Areas
H_2S	0.02 to 5.00	0.005 to 0.050
CS_2	0.07 to 0.37	0.025 to 0.045
CH_3SCH_3	No data	0.042 to 0.062
OCS	0.43 to 0.57	0.430 to 0.570
SO_2	1.00 to 1000	0.050 to 0.120

The importance of reducing the amount of sulfur-containing gases in the presence of silver was demonstrated by Bennett et al.[8] A film of 60 Å (angstrom units) was grown in 1 month in normal laboratory air of 42% relative humidity (RH) and 0.2 ppb H_2S. The fact that the film grew slower at night than during the day was attributed to the more than usual number of people in the laboratory and the extra forepumps operating which contained a small amount of H_2S in their pumping oil.[9] The film growth rate was cut in half by storage in an electron microscope room, and storage in a plastic bag with positive nitrogen pressure stopped film growth completely. Samples stored in the latter condition for 2 months showed less than 5 Å film growth, which was attributed to occasional removal of samples from the plastic bag for thickness measurements. It also appears that storing samples in a vacuum of <70 Torr slowed film formation. Bennett's evaporated silver film, (1,1,1) plane, although less reactive than thermally etched or polished silver surfaces, demonstrates that reducing the amount of sulfur-containing gases is of primary importance in reducing the sulfidation rate of silver. In a static gas flow situation, once the original corrosive gas is depleted, the film growth stops.

Increasing the % RH clearly accelerated the tarnish growth rate, as shown in Fig.1, where the thickness is plotted as a function of total exposure defined as parts per million H_2S times hours exposed. Since each paper used a different analytical technique (scanning electron microscope with energy dispersive x-ray,[10] x-ray fluorescence,[4] radioactive H_2S^{35},[1] and electrolytic reduction[16]) to measure the sulfide film thickness, some discrepancy in the

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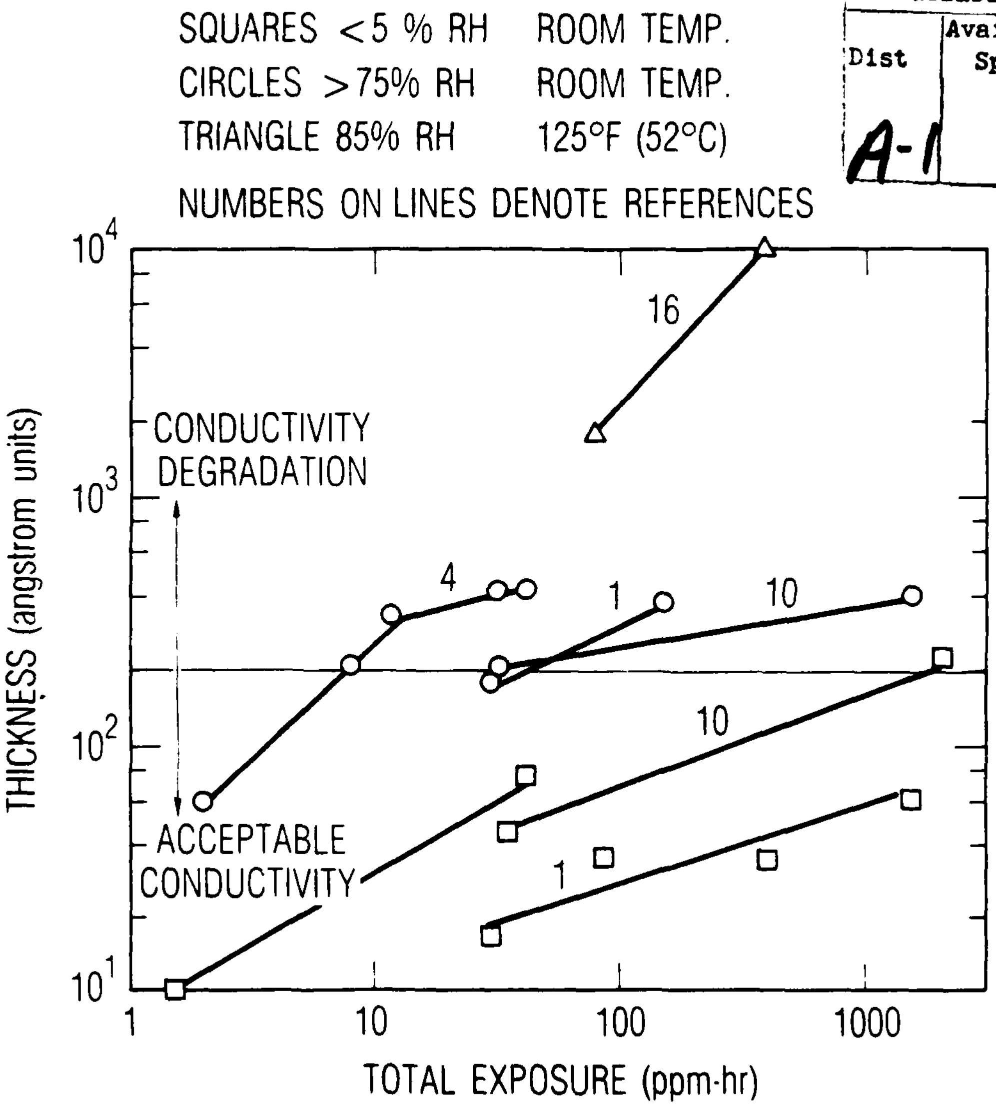

Figure 1. Silver Sulfide Growth as a Function of Total H_2S Exposure and Humidity.

rate of formation is to be expected. Emphasis should therefore be directed toward comparing the high and low humidity results within each paper. A reduction from 75% RH to <5% RH should lower the growth rate by a factor of 3 to 10 times. Pope[4] found that the rate of growth was not significantly different between films grown at 0.5 Torr and 2 ppm water vapor, ~3% RH and ~0.01% RH, respectively; both of these films grew at one-eighth the rate of those at 14 Torr water vapor, ~75% RH, after a total exposure of 30 ppm-hour Using a complex mixture of gases, Rice[5] found tarnish growth to be independent of RH between 30 and 80% RH, whereas Lorenzen[7] found the growth rate to increase significantly between 30 and 50% RH.

B. GROWTH MECHANISM AND ELECTRICAL PROPERTIES

The mechanism for silver sulfidation is not completely understood, but the general belief is that sulfur rather than H_2S is the corrosive constituent that reacts with silver[7] and that water provides an effective medium for the H_2S oxidation to sulfur.[7,10,11] When several monolayers of water are on the surface, the H_2S dissolves easily[12] and dissociates, with sulfur attacking the silver at surface defects such as facets, steps, and edges.[13] In a "dry" surface condition where there is less than one monolayer of water on the surface, the initial step is dissociative adsorption of H_2S onto the metal lattice at a surface defect. OCS is generally noncorrosive under dry conditions at room temperature, but in the presence of water rapidly decomposes.[3] Stoichiometrically, this can be expressed as $OCS + H_2O \longrightarrow H_2S + CO_2$, although the reaction probably has a number of intermediate steps. The mechanism of OCS dry sulfidation is thought to be similiar to the H_2S case.

Silver sulfide tends to grow not as a uniform film but rather as clumps.[11] The clumps per unit area do not change with time but become thicker and grow laterally.[8] Extrapolating these data would indicate that not until 150 Å does the surface coverage become 100%. Initially, sulfur rapidly attacks the silver surface. Once the sulfide layer becomes continuous, growth takes place on the sulfide surface. Thereafter, sulfidation is limited by the rate at which the sulfur-containing gas is supplied to the surface[14] or the rate at which silver, a highly mobile ion,[15] diffuses through the sulfide layer.

Silver sulfide has two crystal forms: β- Ag_2S exists below 177°C, and α - Ag_2S above 177°C. It is an n-type semiconductor with the conductivity increasing with temperature in the β form. Above 177°C, the conductivity increases sharply.

III. CONCLUSION

Most electrical connectors can tolerate some sulfide on their surfaces. Although the thickness at which tarnish begins to noticeably degrade the electrical properties of the circuit is not well established, 200 Å can be considered a reasonable thickness where conductivity problems can begin for the following reasons:

1. The silver sulfide layer becomes continuous at about 150 Å.
2. Silver sulfide grown on a <u>pure</u> silver surface is soft and malleable, being easily pushed aside even under low load. This would allow enough microasperity contacts to give a low contact resistance.[12]
3. Tests examining the electrical conductivity of silver sulfide,[14,16,17] although widely varying, seem to indicate that 200 Å would be a reasonably conservative estimate of the thickness at which electrical properties begin to deteriorate.

Reducing the amount of sulfur gas is of primary importance in slowing or eliminating the growth of the corrosion film. Failure to reduce or minimize the growth of the corrosion film on satellite components where silver is the major constituent can lead to a system failure, e.g., electrical contacts for power or signal slip-ring units. Methods to reduce the sulfur gas concentrations can range from placing the satellite in a chamber with a positive nitrogen flow; placing it in a soft vacuum <70 Torr; or placing it in a purged, sealed chamber. Decreasing the water vapor, % RH, will also reduce the growth rate of the sulfide films, although it is not clear at what % RH an improvement begins. Indications are that at <30% RH the rate of film formation begins to decrease. If the storage environment has been characterized (H_2S concentration and % RH), then Fig. 1 can be used to calculate the approximate "safe" storage time where the electrical contact performance remains acceptable.

Equally important as the storage time after assembly are the prestorage environmental conditions present during the manufacturing, assembly, and storage in stock of the electrical connectors. It is stressed that these results are only applicable to sulfidation on pure silver surfaces. Sulfidation of silver alloys will most likely give different results, since the products of the sulfided alloys have different electrical and hardness characteristics.

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