

Engineering Notes

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Sulfide Corrosion of Silver Contacts During Satellite Storage

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Introduction

INCREASING delays are expected in satellite launchings, requiring satellites to be stored on the ground for possibly up to six years. In some instances, electrical "scratchy" noise on pure silver electrical connectors develops in as little as six 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.

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 Carbonyl sulfide 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.

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 was grown in one 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 operating forepumps, 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 two months showed less than 5 Å film growth, and this was attributed to the 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 percentage 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. Because each paper used a different analytical technique (scanning electron microscope with energy dispersive x ray,¹⁰ x ray fluorescence,⁴ radioactive H_2S ,³⁵ and electrolytic reduction¹⁶) to measure the sulfide film thickness, some discrepancy in the 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 to <5% RH should lower the growth rate by a factor of three to ten times. Pope et al.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-h. Using a complex mixture of gases, Rice et al.⁵ found tarnish growth to be independent of RH between 30 and 80% RH, whereas Lorenzen⁷ found the growth rate to increase significantly between 30 and 50% RH.

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 silver⁷ 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 easily¹² 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. Carbonyl sulfide is generally noncorrosive under dry conditions at room temperature but in the presence of water rapidly decomposes.³ Stoichiometrically, this can be expressed as $\text{OCS} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{S} + \text{CO}_2$, although the reaction probably has a number of intermediate steps. The mechanism of OCS dry sulfidation is thought to be similar 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 this 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

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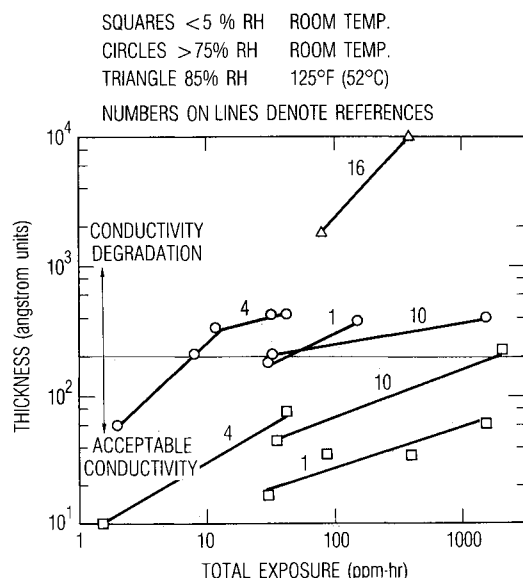


Fig. 1 Silver sulfide growth as a function of total H_2S exposure and humidity.

Table 1 Concentration of atmospheric sulfur gases, ppb

Species	Urban, industrial areas	Remote areas
H_2S	0.02–5.00	0.005–0.050
CS_2	0.07–0.37	0.025–0.045
CH_3SCH_3	—	0.042–0.062
OCS	0.43–0.57	0.430–0.570
SO_2	1.00–1000	0.050–0.120

surface¹⁴ 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.

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 pure 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, percentage RH, will also reduce the growth rate of the sulfide films, although it is not clear at what percentage 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 percentage 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 most likely will give different results, since the products of the sulfided alloys have different electrical and hardness characteristics.

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