

Conductive silver-epoxy pastes: characteristics of alternative formulations

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Conductive silver-epoxy formulations containing 52 and 62 wt % silver flakes have been prepared and exposed to corrosive environments simulating as much as several decades of typical field exposure. The samples were then analysed by a variety of techniques and the results compared with previous data on pure silver and on a 72 wt % formulation. The corrosive sulphur gas diffused readily into the formulations to form silver sulphide at the surface of the flakes. Contact resistance values initially decreased with time, apparently as a result of softening and increased conductivity of the formulations due to water vapour adsorption. Contact resistance values were lower for high humidity exposure in the presence of H_2S than in its absence, suggesting that the effect of water sorption is enhanced by dissolved H_2S . The results indicate that low contact resistances and stable electrical performance are not reached within reasonable field lifetimes for these formulations, even though their characteristics are not markedly affected by corrosive environments.

1. Introduction

Conductive polymers are prepared by mixing electrically conducting fillers into suitable polymeric formulations. The resulting materials function as inexpensive switch contacts and printed circuit board component adhesives. In order to optimize the design and use of these materials, we have been involved in a programme to examine the behaviour of conductive polymers under field-use conditions (high humidity, corrosive environments, etc.). In an earlier paper [1], we compared the performance in corrosive environments of pure silver with that of a conductive epoxy paste containing 72 wt % silver flakes. Among the results were (a) although the contact resistance of the bulk silver is initially much lower than that of the conductive paste, it increases much more rapidly with long exposure to corrosive atmospheres than that of the paste; (b) the epoxy matrix is a reasonably effective barrier to permeation of corrosive gases into the paste; and (c) silver flakes projecting outward from the surface of the paste have little or no resin coating; thus corrosion occurs readily at the surface of the material.

Although silver-epoxy formulations similar to

that previously tested are generally satisfactory in field service, formulations with somewhat lower silver content are also conductive and offer the prospect of decreased silver use and hence lower cost. In the present work, we have studied the morphology and performance of formulations containing 62 and 52 wt % silver, both prior to and following exposure to corrosive atmospheres. A battery of analytical techniques was employed to investigate different properties of the materials: scanning electron microscopy (SEM), energy-dispersive X-ray analysis (EDXA), contact resistance determination, electron spectroscopy for chemical analysis (ESCA), and low-energy ion scattering spectrometry (LEISS). The techniques are described in Section 2 of this paper, as are the sample preparation and exposure procedures. The results are presented in Section 3, and discussed in Section 4.

2. Experimental methods

2.1. Silver-epoxy samples: preparation and properties

The samples used in these studies were formulated from a mixture of epoxy resins, cured with an

TABLE I Electrical resistivity of silver-epoxy paste samples

Silver (wt %)	Silver (vol %)	Bulk resistivity (Ω cm)
52	11	> 1
62	15	> 10^{-2}
72	22	$\sim 1 \times 10^{-4}$

equal amount of a compound prepared from an adduct of two acid anhydrides and a diepoxide. Resin and curing agent contained equal amounts of DuPont V-9 silver "powder". The particles making up the powder are shown by SEM studies to have typical dimensions of 0.5 to $5.0 \mu\text{m} \times 1.0 \mu\text{m}$, with typical thicknesses of $0.05 \mu\text{m}$. For comparison with the previous studies in which 72 wt% of silver powder was used [1], the samples used in the present work contained either 62 wt% or 52 wt% of silver powder.

Specimens of prepared formulation on ordinary window glass were used for LEISS, ESCA, SEM and contact resistance measurements. The glass, in strips ~ 12.5 mm wide by ~ 15 cm long, previously scored for easy breaking into approximately square pieces, was washed thoroughly in warm Alconox solution, rinsed in distilled water and dried using oil-free compressed air. Pressure-sensitive cellophane tape was laid lengthwise over the glass from end to end. Two razor cuts were made lengthwise in the tape, from end to end, and the centre section peeled away to expose the glass. Prepared formulation was forced into the opening using the edge of a clean microscope slide as a squeegee, so that the top surface of the paste was smooth and level with the remaining tape, which was then peeled away. The samples were cured by placing them on a metal plate in a pre-heated circulating air oven at 150°C for 32 min. The cured samples were stored in a vacuum desiccator. Specimens were taken by carefully breaking off approximately square sections from the strips along the score marks.

The electrical properties of the samples, together with that of the previously studied 72 wt% formulation, are shown in Table I. It can be seen that the 72 wt% formulation has satisfactory bulk resistivity, that of the 62 wt% formulation is marginal, and that of the 52 wt% formulation unsatisfactory.

2.2. Exposure of samples

The corrosive environment to which the samples

were exposed consisted of controlled amounts of hydrogen sulphide (H_2S) in pre-purified, humidified air. Hydrogen sulphide was used because it has been shown to be a common atmospheric trace gas which readily corrodes silver [2, 3]. The exposure chamber apparatus includes provisions for monitoring the temperature, dew point, and H_2S concentration on a continuous basis. Each sensor was sampled periodically throughout the exposure period and the resulting values were logged and analysed by a dedicated desktop computer. The exposure system is described elsewhere in more detail [4].

2.3. Contact resistance measurement

Contact resistance (R_c) values were determined by Holm's wire probe method [5], using a modified microhardness tester designed to apply the contact load without appreciable relative sliding motion between the movable arm holding the probe wire and specimen being measured, and thus preventing mechanical damage to any tarnish films that may be present. The probe was a 0.5 mm diameter pure gold wire, applied with a contact load of 100 g. Resistances were measured with a Keithley milliohmmeter whose circuitry assures an open circuit voltage of < 20 mV, preventing electrical breakdown of tarnish films.

2.4. Measurement of silver sulphide thickness

The amount of sulphur incorporated into the conductive pastes was determined with a Kent-Cambridge Stereoscan 2A SEM equipped for energy-dispersive X-ray analysis. The ratio of intensities of the silver and sulphur X-ray signals is a function of the amount of sulphur in each sample. For corrosive film thickness measurements, standard samples are used to define a calibration curve by which thicknesses are determined [6]. The development of such a curve for silver is described elsewhere [7]. The resulting value represents an amount of incorporated sulphur equivalent to that in a film of silver sulphide of the indicated depth upon pure silver.

2.5. ESCA analysis

ESCA measurements of the near surface region were obtained with a PHI Model 548 electron spectrometer, using $\text{MgK}\alpha$ (1253.6 eV) radiation, and a double pass cylindrical mirror analyser (CMA). Spectra were collected in a retarding mode

at a pass energy, E_p , of either 50 or 100 eV. The spectrometer resolution for $MgK\alpha$ X-rays at $E_p = 50$ eV was 1.3 eV (full width at half maximum of Au $4f_{7/2}$ photopeak). The CMA imaged source area was ~ 3 mm in diameter. For the photoelectron kinetic energies encountered with these samples, the signal was extracted from the top 5 to 6 nm of the surface region. System pressures were typically in the range 1 to 3×10^{-9} torr during data collection.

2.6. LEISS analysis

Low-energy ion scattering spectrometry makes use of elastic binary collisions of < 10 keV rare gas ions (He, Ne or Ar) with surface atoms to provide energy spectra characteristic of the atomic mass of the scattering centres. This information can be used to determine the composition of the outermost atomic layer of a solid regardless of its conductivity to a detection limit of ≈ 0.1 at%. By the use of controlled ion-bombardment etching (sputtering), profiles of the distribution of the elemental constituents as a function of depth can be determined. The sample spot size was ~ 1 mm in diameter; the maximum penetration depth studied in these experiments was 30 nm. The instrumental response was not quantitative, but profiles for the respective samples could be compared on a relative basis. The method is described elsewhere [8, 9] in more detail.

3. Results

3.1. Sulphur incorporation

Nine samples each of the 52 wt% and 62 wt% formulations were exposed to the corrosive environment and withdrawn after varying exposure times. Equivalent silver sulphide thicknesses were then determined by SEM/EDXA. Each sample was measured twice and the average taken; typical variations between the two measurements were of order 20%. The results are plotted in Fig. 1, to which are added data on pure silver [7] and on the 72 wt% epoxy formulation previously tested [1]. Several features of the data deserve mention. First, the sulphur incorporated into any of the formulations is significantly less than that in the tarnish film on pure silver. Second, at low exposures the sulphur incorporation is lower on the formulation with 52 wt% silver than on that with 62 wt% silver. Third, at longer exposures the sulphur content is similar on all three paste formulations. This uniformity occurs at exposures

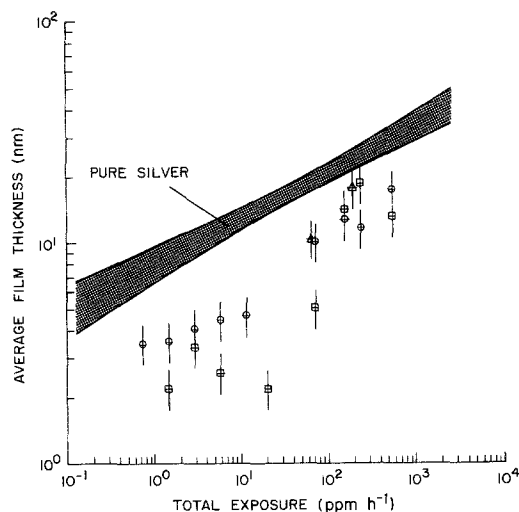


Figure 1 Silver sulphide equivalent film thicknesses for different conductive pastes as functions of total exposure [the product of time and H_2S concentration (parts per million)]. \square 52 and \circ 62 wt% pastes from the present study. Those for \triangle 72 wt% paste and for bulk silver are from previously reported work [1, 7] and are shown here for comparison. The domain shown for pure silver is the area bounded by the 90% confidence limits for a least-squares fit to a large body of silver sulphidation data.

greater than about 100 ppm h. All data refer to the upper $1 \mu m$ of the samples, the approximate depth examined by the EDXA technique.

3.2. Contact resistance

After the nondestructive SEM analyses described above, the contact resistance of the samples was measured. The results are shown in Fig. 2, together with the 72 wt% formulation results derived previously [1]. Two characteristics are noteworthy: the contact resistance is a very strong function of the silver content, and the R_c values for the two formulations with lower silver content decrease with increasing exposure before reaching relatively stable values at about 100 ppm h exposure. These data refer to approximately the upper $5 \mu m$ of the samples, the approximate depth examined by the contact resistance probe [1].

To investigate whether the effects seen above were the result of exposure to H_2S at high humidity or merely to high-humidity exposure (the epoxy is known to adsorb water vapour), matching experiments were made with samples exposed to air without H_2S at 95% r.h. The contact resistances decreased immediately following exposure to a very humid atmosphere. As the samples desorbed

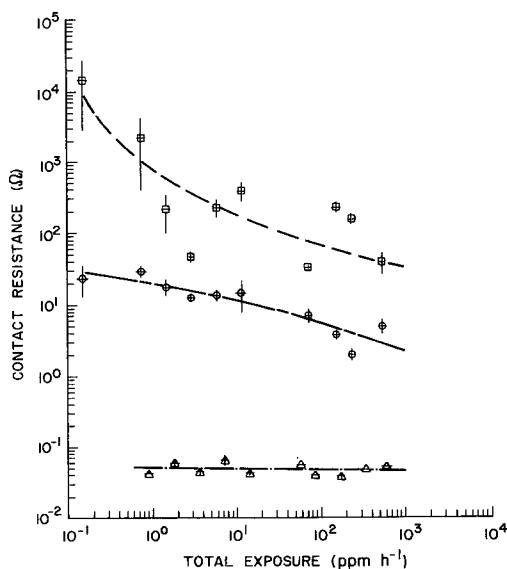


Figure 2 Contact resistance of different conductive pastes as functions of corrosive gas exposure. \square 52 and \circ 62 wt % pastes from the present study; \triangle 72 wt % from previous work [1]. The exposure conditions were: $[\text{H}_2\text{S}] = 2.90 \pm 0.14$ ppm, $T = 20.9 \pm 1.0^\circ\text{C}$, r.h. = $88 \pm 5\%$.

water in laboratory air at 45% r.h. following the exposure, the contact resistances increased. In all cases, the structural integrity of the samples exposed to H_2S in humid air was less than for those samples exposed to H_2S alone (i.e. they were "softer"). In addition, there was some tendency for H_2S exposure to produce lower contact resistances, although the lack of firmness made contact resistance readings difficult to obtain.

3.3. ESCA analysis

Three samples each of the 52 wt % and 62 wt % formulations were used for ESCA analysis. One pair was retained as an unexposed sample, a second pair was exposed to the corrosive environment for 73 ppm h, and a third pair exposed for 517 ppm h. X-ray core-level photoemission spectra were then obtained for all samples. The results are shown in Table II, the numbers being considered accurate to about $\pm 20\%$.

The unexposed samples contain no detectable sulphur. The carbon and oxygen signals are largely due to the epoxy, although some surface C and O contamination is probably present as well. After exposure, the samples are characterized by the appearance of a sulphur signal, which in all cases is about 2% of the silver signal on the peak height scale. As found in previous work, the binding

TABLE II Elemental peak heights from ESCA examination of conductive pastes

Sample	Ag	S	C	O
52 wt %, unexposed	142	—	50	58
62 wt %, unexposed	520	—	50	60
52 wt %, moderate exposure*	1100	24	42	56
62 wt %, moderate exposure	3000	51	31	33
52 wt %, long exposure†	1000	22	40	45
62 wt %, long exposure	3600	62	28	34

* 73 ± 3 ppm h exposure to H_2S in humidified air.

† 517 ± 24 ppm h exposure to H_2S in humidified air.

energy of the sulphur is consistent with the compound Ag_2S .

Two features of the silver and sulphur results should be noted. First, there is no significant change in either the silver or sulphur signals for the 52 wt % formulation between the 73 ppm h exposure and the 517 ppm h exposure. An increase, though a relatively small one, does occur for the 62 wt % formulation. In each case, the initial silver signal increases by a factor of 6 to 7 following exposure to the corrosive atmosphere. These results apply to the top 5 nm of the sample, since that is the approximate depth examined by the ESCA technique.

3.4. LEISS analysis

Three samples each of the 52 and 62 wt % formulations, exposed concomitantly with the ESCA samples, were used for the LEISS analysis. Samples were sputtered for 75 to 90 min and analysed throughout for silver and sulphur signals. The relative magnitudes of the silver signals in the different samples were quite close to that expected on the basis of the volume percentage of silver in the formulation (Table I). The ratios of LEISS silver to sulphur signals for the samples are shown in Fig. 3. For the 52 wt % paste, the data show low silver levels near the surface of the sample, followed by an increase to a relatively constant ratio at 5 nm depth (15 min sputter). The sulphur has thus diffused into the epoxy to a depth of at least 30 nm. The sample exposed for a longer period of time has acquired about one-third more sulphur than that exposed for the more moderate period (i.e. the Ag/S ratio of the former is lower than that of the latter). For the 62 wt % paste similar features are seen in the data, except that the sample exposed for a longer period has somewhat higher sulphur concentrations near the surface.

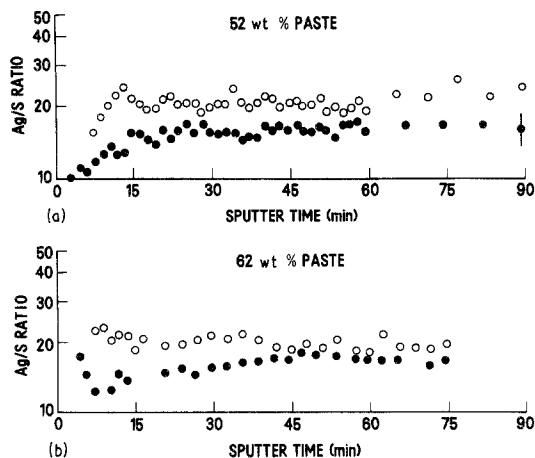


Figure 3 (a) The LEISS silver to sulphur ratios as functions of sputter time (arbitrary depth) for 52 wt % paste samples exposed to the corrosive atmosphere. The sputter rate is not well calibrated, but is approximately 0.3 nm min^{-1} . \circ samples with moderate exposure; \bullet samples with long exposure. The magnitude of the estimated errors in these determinations is indicated on the last filled circle. (b) The LEISS silver to sulphur ratios as functions of sputter time (arbitrary depth) for 62 wt % paste samples exposed to the corrosive atmosphere.

By combining the ratio results of Fig. 3 with the absolute silver signals, it can be calculated that the sulphur incorporation of the 62 wt % paste is about twice that of the 52 wt % paste for the moderate exposure and about 1.5 times that of the 52 wt % paste for the long exposure. These results are all consistent with the SEM/EDXA results of Fig. 1.

4. Discussion

The measurements of electrical properties of the materials we have examined suggest that formulations containing $\sim 72 \text{ wt } \%$ ($\sim 22 \text{ vol } \%$) silver powder provide satisfactory interior conductivity and contact performance. Formulations with 62 wt % ($\sim 15 \text{ vol } \%$) silver powder offer marginal electrical performance; those with 52 wt % (11 vol %) silver powder are unsatisfactory. Apparently the probability of contact between adjacent silver flakes becomes low as the volume percent decreases below about 15 to 20 [10, 11], although the flake geometry plays an important role in establishing this limit [12, 13], as does the presence of organic dispersers on the flake surfaces [14].

The initial contact resistances of the formulations decrease by about a factor of a hundred

for each ten weight percent of silver added past 52 wt %. Exposure to high humidity for periods as short as a day, either with or without concomitant H_2S , results in a marked decrease of R_c for the 52 wt % and a small decrease for the 62 wt % formulations. Evidence from the ESCA analyses suggests that this behaviour results from an increased level of surface silver, as well as from the increased conductivity provided by the sorbed water vapour. (The latter effect has previously been seen in contact resistance measurement of metals covered by deliquescent films [15].) The particles of silver powder are too large to migrate intact; it seems likely that individual silver atoms are diffusing through voids opened by water sorption, just as metal atoms diffuse upwards through corrosion films [16], and that water sorption is enhanced by dissolved H_2S . The induction time for the metal diffusion to become operative is of the same order of magnitude as the time for water vapour to be sorbed into the epoxy matrix [17].

Except for some near-surface variation, the concentration of sulphur-containing molecules incorporated into the formulations are shown by LEISS to be relatively constant to a depth of at least 30 nm. The SEM/EDXA data, which probe far deeper, indicate that for the longer exposures the sulphur content is sufficient to sulphidize the silver to at least twice that depth. Unlike a solid silver surface, where the presence of a tightly-adhering tarnish film strongly decreases conductivity [1], the silver epoxy formulations show much more stable electrical behaviour over extended periods of exposure. This behaviour does not appear to be due primarily to corrosion resistance, as suggested by Tamai [18], since corrosive gases are gradually absorbed into the formulations. Rather, the geometry of silver-epoxy formulations allows conduction to occur within a silver flake path whose external surfaces are partially sulphidized, or to permit contact probes to create conduction paths by compacting the upper few micrometres of the material.

Finally, we relate our experiments to the case of exposure of silver epoxy formulations in field use. The dependence of conduction on humidity has the potential to render marginal epoxy formulations satisfactory in field environments where the humidity is very high. Of special interest in this context is the instability of contact resistance values during the initial stages of sulphidation.

We have noted that the R_c values for these relatively silver-poor formulations stabilize after an exposure of about 100 ppm h. This is, however, equivalent to a field exposure of *ca* 10y in a city environment [19]. Few products utilizing conductive silver-epoxy paste will be designed for longer lifetime and thus may not be within a regime of stable performance as a contact material.

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