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The morphology and corrosion resistance of a conductive silver–epoxy paste

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Among the important properties of conductive silver—epoxy pastes are their relatively low internal electrical resistance and their low rate of sulphidizing relative to pure silver. To investigate these properties in more detail and to gain understanding of the physical mechanisms involved, paste and bulk silver samples have been exposed to a controlled corrosive atmosphere of hydrogen sulfide and water vapour in purified air. The exposed samples were then analysed by a variety of surface and bulk techniques. The results demonstrate that (1) 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; this is especially true at low contact probe forces, (2) the hydrogen sulfide permeation constant through a free-standing film of unsilvered paste is $(7.0 \pm 0.3) \times 10^{-2}$ barrers†: sufficiently low that transport of H_2S into the bulk paste is strongly inhibited, (3) silver flakes projecting outward from the surface of the paste have little or no resin coating. Corrosion thus occurs on the surface of the material but is inhibited within the material. The relative softness of the material allows contact probe penetration into the uncorroded bulk matrix. As a result, little decrease in the conductivity of the paste occurs even after extended exposures to a corrosive environment.

1. Introduction

Conductive polymers, prepared by mixing electrically conductive fillers into a suitable polymeric formulation, are widely used in applications such as low-cost switches [1] and printed circuit board component adhesives [2]. Despite this utility, a complete mechanistic understanding of the behaviour of these materials has not been achieved. It is thought that the conductive fillers, which are generally metal flakes, form a continuous metallic conduction path [3, 4]. This may not be true in all such systems, however [5]. Another area of uncertainty is the formation of a coating of resin on the metal flakes, a coating which may always be present [6] or whose presence may be a strong function of temperature [4]. A further property of conductive polymers that is of interest is their relatively good resistance to corrosion, even for flake metals that are quite corrosion susceptible in the bulk [1]. Studies [7] have shown that the contact resistance of silver-filled paste, although initially ~ 50 times that of bulk silver, increases much more slowly when it is exposed to sulphidizing environments. In fact, results from previous studies, confirmed in the present study, show that the contact resistance of bulk silver can become one to two orders of magnitude higher than that of a silver-filled paste after exposure in the same sulphidizing environment.

Among the mechanistic questions raised by the behaviour outlined above are the following:

(1) What is the nature, i.e. composition and morphology of the surface region of a conductive polymer? Is the silver particulate covered with a

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†1 barrer = $(1 \times 10^{-10}$ cm^3 permeant · cm thickness)/(cm^2 area · cm pressure · sec).

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thin layer of the resin? Can this resin inhibit contact of the sulphidizing material (e.g. H_2S) with the silver particulate?

(2) What is the basis for the different contact resistance behaviour of conductive silver-filled polymers and of bulk silver?

(3) What is the basis for the different corrosion rates of conductive silver-filled polymers and of bulk silver?

(4) What is the permeation rate of H_2S in the cured epoxy resin matrix (i.e. are the properties of the conductive polymer attributable to a very low permeation rate)?

In an attempt to answer these questions, an experiment was devised that applied a number of different analytical techniques to the study of a conductive polymer. The material, described below and hereafter referred to as the "paste", was developed for electrical contact applications. It is similar in formulation to conductive polymers used as component adhesives, and seems a suitable "typical" conductive polymer. The following tests were performed:

(a) Exposure of silver-filled and unfilled paste samples and of bulk silver to a corrosive environment containing hydrogen sulphide gas in wet air.

(b) Measurement of the contact resistance of the silver-filled paste and bulk silver samples as functions of exposure time and probe load.

(c) Determination of the S/Ag X-ray intensity ratio as a function of exposure time by energy-dispersive X-ray analysis (EDAX), using a scanning electron microscope (SEM) equipped with an X-ray detection system.

(d) Examination of the surface of the paste by low-energy ion scattering spectroscopy (LEISS) and electron spectroscopy for chemical analysis (ESCA) to determine its composition, and by SEM to determine its morphology.

(e) Examination by SEM of regions of the paste surface subjected to contact resistance probing for evidence of morphological changes (e.g. damage, deformation, penetration).

(f) Measurement of the permeation rate of H_2S through films of the cured, unfilled, epoxy resin matrix.

In Section 2 the sample preparation and analytical procedures are described. The results are presented in Section 3. The schematic picture of the conductive paste that emerges from these analyses is presented and discussed in the final section of this paper.

2. Experimental section

2.1. Properties and preparation of conductive paste samples

The conductive paste used for our experiments (BTL 6) consists of a mixture of epoxy resins, cured with an equal weight of a compound prepared from an adduct of two acid anhydrides and a diepoxide. Both resin and curing agent contain 72 wt% ($\sim$20 vol%) of DuPont V-9 silver "powder". SEM studies of the latter show that the maximum dimension (length) of the particles ranges from 0.5 to 5.0 μm (agglomerates), with most particles being about 1 μm in length.

Specimens of BTL 6 on ordinary window glass were used for LEISS, ESCA, SEM and contact resistance measurements. The glass, in strips $\sim$ 12.5 mm (0.5 inch) wide by $\sim$ 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 BTL 6 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 preheated circulating air oven at 150° C for 32 min. The cured samples were stored in a vacuum dessicator. Specimens were taken by carefully breaking off approximately square sections from the strips along the score marks.

Comparison samples without silver flakes were made in two ways. For LEISS, ESCA and SEM analyses, the samples were prepared as outlined above, using a formulation identical to BTL 6 but without silver. For the permeation experiments, free-standing films were prepared by casting films of the polymer between copper sheets using a Mylar spacer. The samples were cured for 30 min at 150° C (actual film temperature) and films were obtained by dissolving the copper in 1 : 1 aqueous nitric acid.

The bulk silver samples were 99.999% pure, and were mechanically polished [8] to a surface roughness (as determined by SEM examination) of $\leqslant 0.6\ \mu$m.

2.2. Sulphidation of samples

The samples were exposed to H_2S using an experimental arrangement previously devised and described in detail by Franey *et al.* [9]. Control of the H_2S concentration in the chamber was achieved by the polymer valve technique [10]. The water content of the air was varied by adjusting the portion of the air supply that passes through the humidifier. A dew point hygrometer and hot wire anemometer monitored the dew point and flow rate continuously. An important feature of the system is the provision for continuous analysis of the H_2S concentration, which eliminates the potential for undetected concentration reductions resulting from H_2S loss to wet chamber walls or other surfaces. Each sensor was sampled once per minute throughout the exposure period; the resulting values for the exposure conditions are derived from statistical analysis of these data with a dedicated desktop computer.

2.3. Contact resistance measurement

Contact resistance (R_c) values were determined by the wire probe method [11]. The probe was a 0.5 mm diameter pure gold wire, applied at contact loads of 1 to 100 g. Resistances were measured with a Keithley milliohmmeter.

2.4. Sulphide film measurement

The morphology of the sulphide films was studied with a Kent-Cambridge Stereoscan 2A SEM. Via energy-dispersive analysis of X-rays, the instrument was also used to measure the intensities of silver and sulphur X-ray signals from the various samples. The ratio of these intensities provides a determination of the relative amount of sulphur incorporated into each of the samples during exposure. The data were obtained from an area of $\sim 1\,\text{mm}^2$.

2.5. ESCA analysis

ESCA measurements of the near surface region were obtained with a PHI Model 548 electron spectrometer, using MgKα (1253.6 eV) radiation, and a double pass cylindrical mirror analyser (CMA). Spectra were collected in a retarding mode at a pass energy, Ep, of either 50 or 100 eV. The spectrometer resolution for MgKα X-rays at $E\text{p} = 50\,\text{eV}$ 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 50 to 60 Å of the surface region. System pressures were typically in the range 1 to 3×10^{-9} Torr during data collection.

2.6. LEISS analysis

LEISS is described in detail by Honig and Harrington [12] and Smith [13]. In brief, the method 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 ~ 300 Å. The instrumental response was not quantitative, but profiles for the respective samples could be compared on a relative basis.

2.7. Permeation measurements

The permeation constant for the epoxide film was measured by dynamic gas detection techniques which permit H_2S to permeate the film under the realistic conditions of atmospheric pressure and the simultaneous presence of oxygen, nitrogen and carbon dioxide in standard atmospheric proportions. The technique has been described in detail previously [14].

3. Results

3.1. Contact resistance

Samples of both bulk silver and paste turned medium to dark grey upon exposure, thus qualitatively demonstrating the tendency towards sulphidation of the two materials. A more quantitative measurement, the contact resistance values as a function of exposure time, is shown in Fig. 1 for probe loads of 100 g. Two characteristics of earlier experiments [7] are confirmed: that the R_c values for the paste are much higher initially than those for bulk silver, and that bulk silver R_c values degrade much more rapidly at long exposure times. At the lesser exposures, the R_c values for the silver increased slowly with time, a feature best seen in the log–log plot of Fig. 1a. At long exposure times the contact resistance of the silver

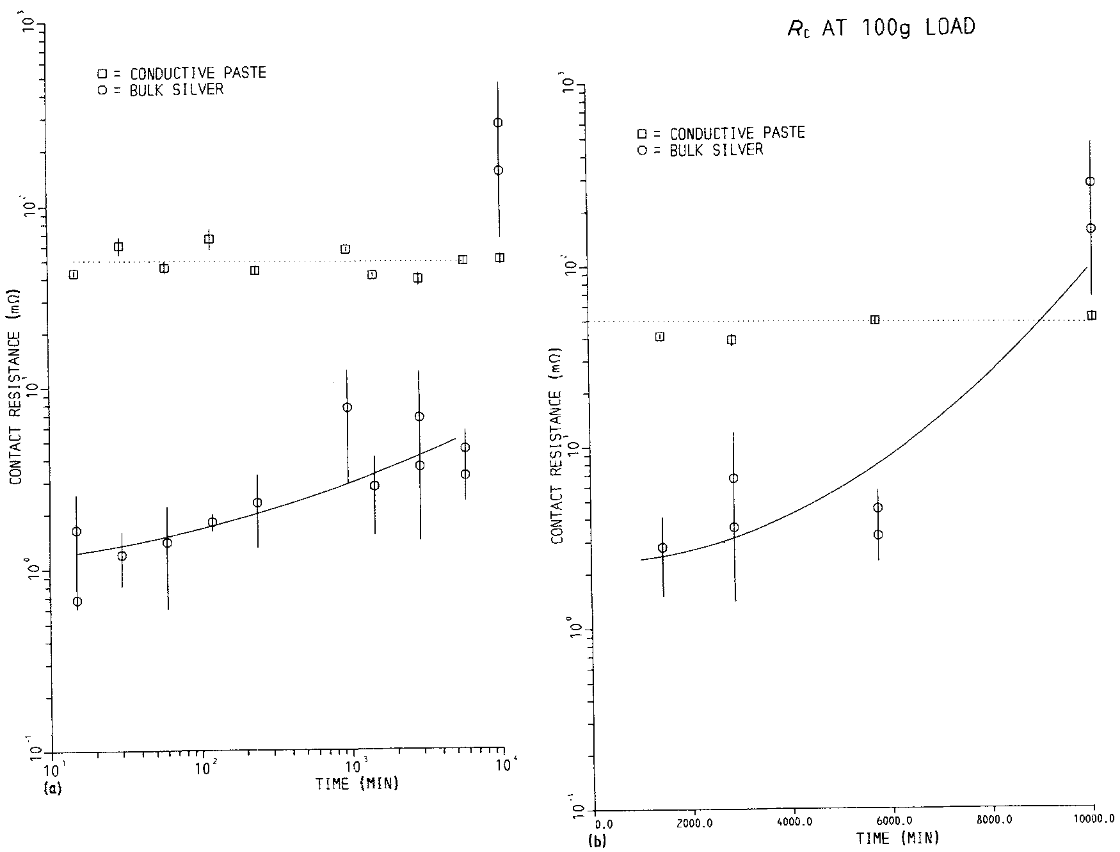


Figure 1 Contact resistance of conductive paste and bulk silver samples as functions of exposure time. The vertical lines on each data point indicate the standard deviation of the four to five measurements whose average defines the contact resistance. The exposure conditions were: $[H_2S] = 2.9 \pm 0.5$ parts per billion (ppb), $T = 21.7 \pm 0.6°$ C, r.h. $= 89 \pm 4\%$ (the standard deviations represent the degree of fluctuations of experimental conditions during the exposure period; by comparison, the measurement errors involved are negligible). The contact probe force used in making these measurements was 100 g: (a) logarithmic abscissa to show short exposure behaviour and (b) linear abscissa to show long exposure behaviour. The lines (which are added to assist the reader) are least-squares linear or quadratic fits to the data.

increased markedly, as seen on the linear–logarithmic plot of Fig. 1b. The paste value remained relatively constant throughout.

A further feature of the plots of Fig. 1 is the magnitudes of the standard deviations. Each plotted data point is the average of four or five measurements, whose standard deviations are indicated by the vertical lines. Those for the paste are quite small, indicating that the sulphidation proceeded uniformly over the sample surfaces. Those for bulk silver were much larger, especially at the longer exposure times. Such behaviour indicates that the silver sulphidation proceeded non-uniformly, being characterized by neighbouring areas with significantly different film formation. It should be noted that with thick sulphide layers (those with $R_c > 100\,\text{m}\Omega$ on the bulk silver samples, the contact resistance decreased as the measurements were being made due to the penetration of the probe through the soft sulphide layer. These measurements are thus most useful in monitoring the initial and intermediate stages of sulphide film formation.

The difference in behaviour between the paste and silver samples was also demonstrated by measurements at different contact probe loads. The results, shown in Fig. 2, demonstrate that the silver contact resistances are quite dependent on the probe load (i.e. the contact "force"); the R_c values for the paste are nearly independent of load.

3.2. SEM analysis

The sulphur to silver X-ray intensity ratios for duplicated samples of exposed paste and bulk silver are given in Table I. These data indicate that sul-

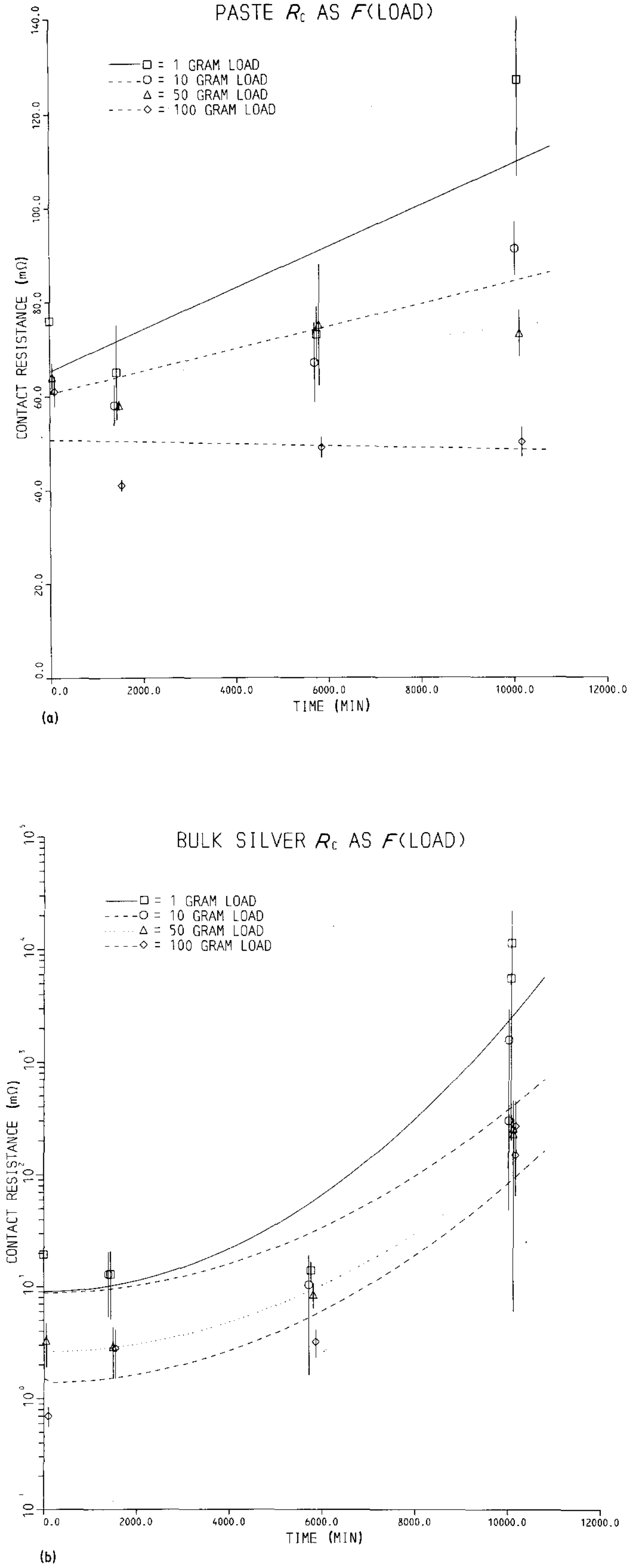


Figure 2 Contact resistance of the samples shown in Fig. 1 as a function of probe load: (a) conductive paste and (b) bulk silver. (Note the change of ordinate scale and type between the two plots.)

TABLE I Sulfur to silver X-ray ratios for exposed samples

Exposure time (min)	Paste		Bulk silver	
	Sample 1	Sample 2	Sample 1	Sample 2
0	< 0.01	< 0.01	< 0.01	< 0.01
1050*	0.02	0.03	0.05	0.05
3210†	0.05	0.05	0.07	0.08

*Exposure conditions were: $[H_2S] = 3.7 \pm 0.6$ ppm, $T = 22.6 \pm 0.3°$ C, r.h. = 90 ± 4%.

†Exposure conditions were: $[H_2S] = 3.6 \pm 1.5$ ppm, $T = 22.5 \pm 1.1°$ C, r.h. = 89 ± 5%.

phur (relative to silver) was accumulated more rapidly by the bulk silver in these exposures. (Some of our earlier work did not illustrate this effect, however. In any case, it will be shown below that the relative electrical performance of the samples cannot be simply described by the amount of sulphur uptake.) This analytical technique measures the integrated signal from approximately the upper 1 μm: it is thus more accurately regarded as a bulk measurement than as a surface measurement.

The visual appearance of the paste sample following contact probing provides a valuable insight into its electrical behaviour. As shown in Fig. 3, the probe penetrates readily into the body of the paste. (The penetration depth shown is of the order of 5 μm.) In contrast to a bulk silver contact, the electrical properties of which are a strong function of the surface properties of the silver, the electrical properties of the paste when used as a contact appear to reflect bulk (or compressional) processes occurring throughout a significant depth.

3.3. ESCA analysis

X-ray core-level photoemission spectra were examined for the following three sets of samples:

(1) Exposed and unexposed surfaces of the pure epoxy binder used in the elastomeric paste.

(2) Exposed and unexposed silver-filled conductive paste.

(3) Bulk samples of pure Ag and Ag_2S.

Comparison of the cured, silver-free paste with a similar film exposed to the H_2S environment for one day failed to reveal any uptake of sulphur as monitored by the sulphur 2p intensity between 160 and 170 eV. In the silver-filled paste, however, exposure to the corrosive environment did lead to a surface tarnish reaction due to the formation of Ag_2S. Silver 3d and suphur 2p core level spectra are shown in Fig. 4 for exposed and unexposed samples of the conductive paste along with a bulk sample of Ag_2S. The spin-orbit splitting of the Ag $3d_{3/2}$ and $3d_{5/2}$ levels is sufficiently large to be individually resolved; the S $2p_{1/2}$ and $2p_{3/2}$ levels are not resolved. The chemical shift in the Ag 3d levels between pure Ag and Ag_2S is of the order of 0.2 eV, thereby making it difficult to identify tarnishing from that signal alone. However, uptake of sulphur is clearly apparent on the exposed conductive paste (in the bottom panel of the figure) and the binding energy of this sulphur is consistent with its assignment as Ag_2S by comparison with a bulk sample (top panel).

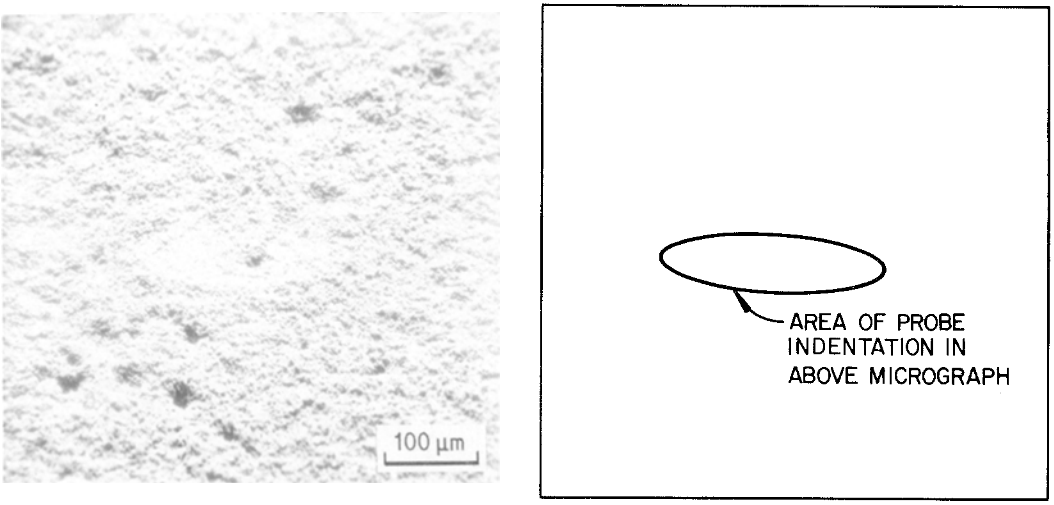


Figure 3 The visual appearance of the conductive paste following contact resistance measurement with the gold wire probe.

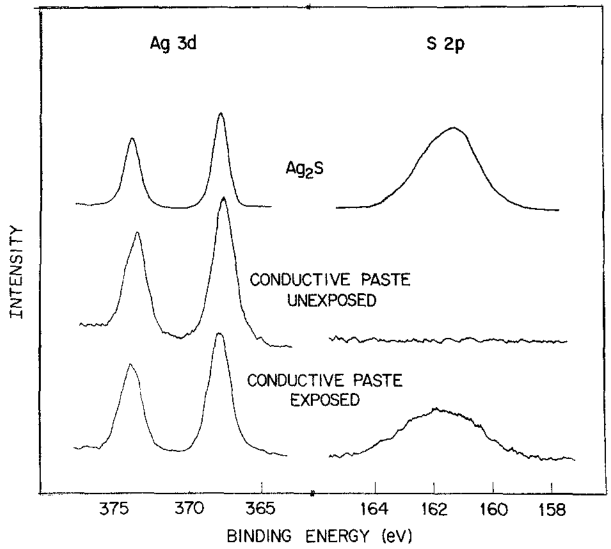


Figure 4 ESCA electron energy spectra for bulk silver sulphide (top panel) unexposed conductive paste (centre panel), and exposed conductive paste. The exposure conditions for the latter were: $[H_2S] = 2.9 \pm 0.5$ ppb, $T = 21.7 \pm 0.6°$ C, r.h. = 89 ± 5%, time = 2880 min.

3.4. LEISS analysis

Composition depth profiles of the Ag/S peak intensity ratios for both bulk silver and conductive paste exposed to the same $H_2S–H_2O$ atmosphere are plotted in Fig. 5. At the onset of sputtering, the Ag/S ratios for both samples have essentially the same value and show the silver concentration at the surface of both samples to be alike. In the case of the corroded bulk silver, the Ag/S ratio remains constant for ≈ 38 min of sputter time (~ 130 Å depth). The flat segment of the curve represents a continuous film consisting primarily of Ag_2S, a conclusion confirmed by ESCA analysis. At progressively greater depths, the Ag/S ratio increased steadily. This gradient is due principally to ion sample beam "edge effect" and does not accurately characterize the width of the metal–sulphide interface.

Conversely, no constant Ag/S value was observed for the corroded paste, indicating the absence of a homogeneous tarnish layer. This observation supports the hypothesis that penetration of sulphur atoms into the paste is a less efficient process than that of Ag_2S film formation on bulk silver. Near the paste surface, where inhibition of H_2S diffusion is unimportant, the Ag/S ratio is similar to that found for the bulk silver, an observation that demonstrates that silver flakes corrode readily only when H_2S is available to them.

Ideally, the area of silver flake exposed at the surface of the paste is calculated to be ~ 20% of the total sample area. The actual distribution of silver at the paste surface can be inferred from the data in Fig. 6. Here, the ratio of the Ag peak intensity for polished bulk silver to that for the corresponding Ag peak intensity found for paste (not corroded) is plotted as a function of sputter time. The profile shows a steady value of ~ 1.1 which means that a much higher than anticipated silver concentration exists at the paste surface (ratio 5.0). It appears that the "squeegee" process

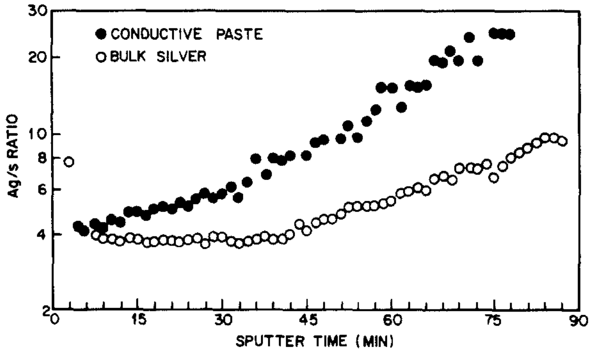


Figure 5 LEISS profiles of the Ag/S ratio in conductive paste and bulk silver samples. The exposure conditions are the same as those given in Table I.

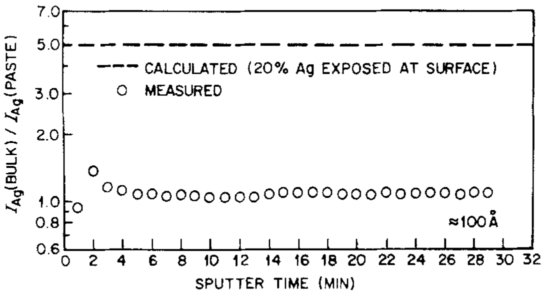


Figure 6 LEISS depth profile ratios of silver intensity from a polished and unexposed bulk silver sample and silver intensity from an unexposed paste sample.

used to form the film concentrates the silver flakes at the surface, while not coating them with an adherent resin film.

3.5. Permeation studies

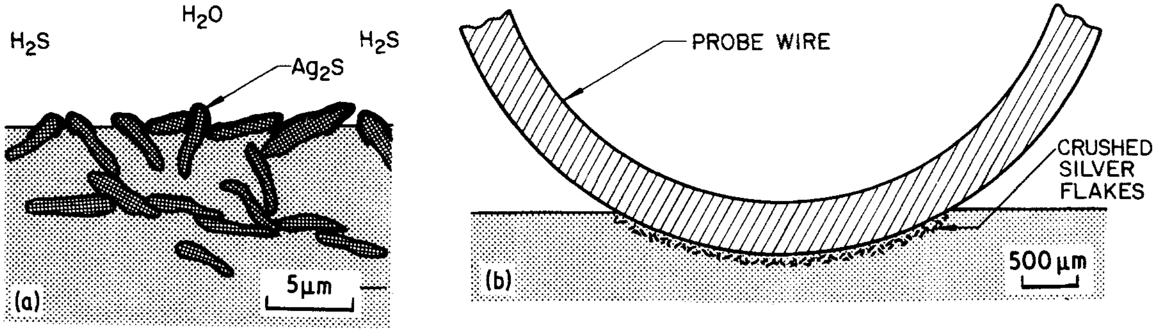
Duplicate measurements of the permeation of H_2S through the free standing paste films give a value for the permeation constant of $(7.0 \pm 0.3) \times 10^{-2}$ barrer*. Epoxides are known to be relatively impermeable to most gases [15, 16] a finding consistent with our measurements. Similar measurements were made for H_2S permeation in a variety of other epoxy polymers [17]; the value derived here falls within the range of those values. The permeation constant measured for the paste is low enough to restrict the transport of H_2S, but not so low as to inhibit it completely.

4. Discussion

The results presented in the previous section provide considerable insight into the mechanism involved in conduction, contact resistance and sulfidation of the conducting paste. Using this information, a schematic picture of the morphology and interaction of the material has been devised. Fig. 7a is a rendering of that picture at high magnification. The silver flakes are seen to be abundant at the surface, in accordance with the LEISS results, and to have no significant epoxy resin coating. This lack of coating is consistent with the conduction of the paste when prepared; if the flakes were readily wetted by the resin their conduction might be nearer that of the pure resin.

The portions of the silver flakes that protrude through the resin surface are readily sulphidized to Ag_2S by the H_2S vapour, as demonstrated by the Ag_2S signal from the ESCA analysis. The flakes just below the surface are sulphidized as well. Further from the surface, the diffusion inhibition of the resin limits the amount of sulphur available to the silver; thus, the corrosion is limited as well.

In Fig. 7b an attempt is made to demonstrate the mechanical deformation involved in contact operation. The probe wire used by us is quite small, yet its diameter is about a factor of one hundred larger than that of the silver flakes. As it comes into contact with the paste it deforms the surface (see Fig. 3), pushing the latter in upon itself. Given the relative impermeability of the paste, the sulphidized silver has been largely confined to the upper few hundred Å, a depth readily penetrated by the probe even at moderate probe loads. Except at very long times (i.e. deep H_2S



(a) (b)

Figure 7 Schematic picture of conduction, contact resistance and corrosion of the conductive paste: (a) side view of surface layer at high magnification and (b) side view of surface layer at moderate magnification.

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*1 barrer = $(1 \times 10^{-10}$ cm^3 permeant · cm thickness)/(cm^2 area · cm pressure · sec).

penetration) and low probe loads, very little degradation of conductivity occurs. Bulk silver, in contrast, forms a relatively adherent film requiring higher probe loads to penetrate.

The results suggest applications for which a conductive paste may be especially advantageous. It is doutbless an environmentally rugged contact material, although its high initial resistance may limit its use. It is particularly appropriate for low contact force applications, in which the contact resistance must be reasonably stable with time. Its use as an adhesive in applications involving corrosive atmospheres is appropriate as well, provided care is taken to select an epoxy resin with good permeation inhibition.

Since only one conductive paste has been examined in detail, our results cannot necessarily be generalized to include the myriad of materials that are available. However, our material bears many of the common characteristics of such materials. It seems reasonable to infer that our results will apply at least qualitatively to many other conductive pastes. In particular, it is anticipated that pastes formulated with copper or tin/lead rather than silver will have similar tarnishing characteristics.

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References

1. M. GROSSMAN, *Elect. Design* **28** (13) (1980) 63.
2. H. STERN, *ibid.* **28** (13) (1980) 105.
3. A. MALLIARIS and D. T. TURNER, *J. Appl. Phys.* **42** (1971) 614.
4. A. LOVINGER, *J. Adhes.* **10** (1979) 1.
5. B. JACHYM, H. SODOLSKI, T. SLUPKOWSKI and R. ZIELINSKI, *Phys. Stat. Sol. A* **24** (1974) K159.
6. F. F. T. DE ARAUJO and H. M. ROSENBERG, *J. Phys. D.* **9** (1976) 1025.
7. L. H. SHARPE and V. TIERNEY, unpublished results (1979).
8. M. E. DAVIS and T. J. LOUZON, *Metallog.* **13** (1980) 195.
9. J. P. FRANEY, T. E. GRAEDEL and G. W. KAMMLOTT, Proceedings of the International Conference on Atmospheric Corrosion, edited by W. H. Ailor, (The Electrochemical Society, Princeton, 1981).
10. J. P. FRANEY, *J. Electrochem. Soc.* **126** (1979) 2159.
11. R. HOLM, "Electric Contacts: Theory and Application" (Springer-Verlag, Berlin, 1967) p. 42.
12. R. E. HONIG and W. L. HARRINGTON, *Thin Solid Films* **19** (1973) 43.
13. D. P. SMITH, *Bull. Am. Phys. Soc.* **14** (1968) 788.
14. T. E. GRAEDEL, J. P. FRANEY, W. H. STARNES, Jr, D. C. HISCHE and P. C. WARREN, *J. Appl. Polymer Sci.* **23** (1979) 1769.
15. R. M. BARRER, J. A. BARRIE and P. S.-L. WONG, *Polymer* **9** (1968) 609.
16. G. A. GORDON and A. RAVVE, abstract paper ACS, 176, ORPL-70, Amer. Chem. Soc. (1978).
17. T. E. GRAEDEL and J. P. FRANEY, abstract paper ACS, 178, POLY-146, Amer. Chem. Soc. (1979).

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