

High Tensile Strength Thick-Film Silver-Palladium Metallisations

IMPROVED COMPOSITIONS FOR SCREEN-PRINTED CIRCUITS

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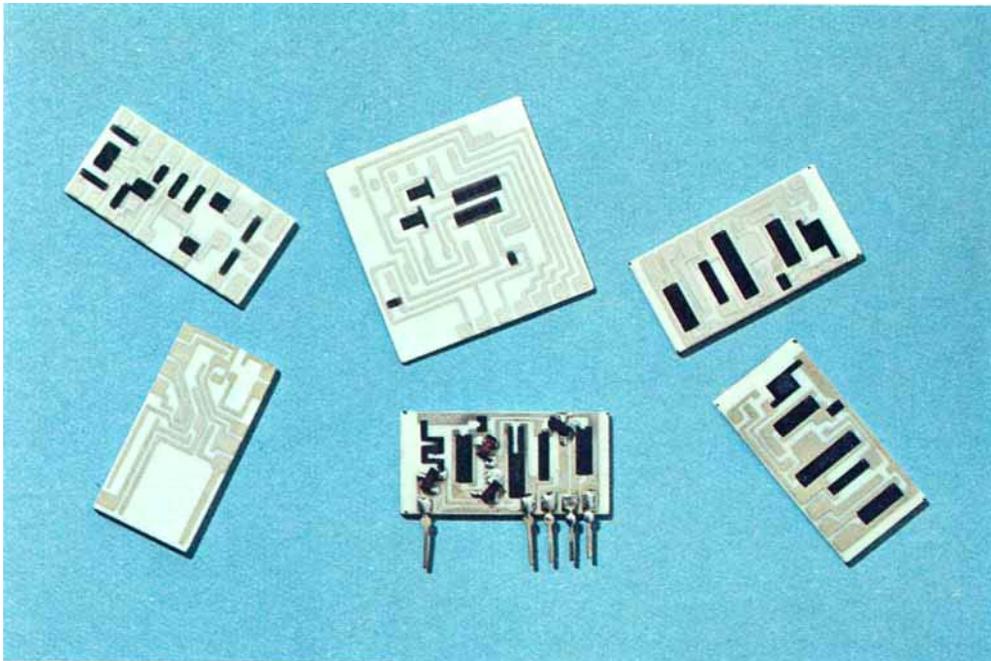
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Thick-film, silver-palladium conductor compositions with improved mechanical properties have been developed in the Johnson Matthey Research Laboratories. These conductors are capable of retaining high adhesion strengths using tin-lead solder after prolonged storage at elevated temperature. This article is based upon a contribution to the Institution of Electronic and Radio Engineers' Conference held at the University of Technology, Loughborough, in September.

The rate of progress in the level of complexity that any electronic technology is capable of accommodating is limited inevitably by the nature and quality of the materials used. At present, this is nowhere more true than in thick-film microelectronics, with advances in recent years made possible by considerable improvements in both the physical and electrical properties of compositions suitable for screen-printing applications. Much of this progress has been concentrated on further miniaturisation of hybrid circuits, not only as space-saving exercises when both weight and size are at a premium, but also to minimise path lengths among devices in order to obtain shortest over-all response times from the circuit. In turn, however, these smaller, more compact assemblies, operating at somewhat higher temperatures, place increasing demands on thick-film materials used in hybrid microelectronics, particularly those which form interfaces or junctions of dissimilar metals in the circuit. These areas, frequently lying in natural, thermal drain paths, represent sites of metallurgical activity potentially detrimental to over-all electrical performances. Such active sites exist at most inter-

connections between thick-film conductors and lead-out wires or frames, and also at areas of attachment for discrete devices. Interactions at these interfaces during operation account for the principal cause of limited life-times of high-density hybrid circuits.

Of all conductor compositions encountered in thick-film networks, those containing silver and palladium are the most widely used (1), offering circuit manufacturers potentially the most attractive compromise between cost and performance. Screen printed silver-palladium films are readily wetted by a range of soft solders, and this property is exploited frequently by circuit manufacturers as a convenient means of overcoming problems associated with multi-device attachment (2). This asset is used with full awareness of limitations in using tin-containing solders with silver-palladium conductors—limitations which were recognised nearly ten years ago and subsequently characterised in an elegant investigation by Crossland and Hailes (3). These workers found that above 125°C there is a rapid diffusion of tin from the solder into palladium-containing metallisations forming brittle intermetallics based



A selection of thick-film networks forming the basis of hybrid amplification circuits and showing the extensive use of screen-printed silver-palladium conductors. The fired conductors readily accept solder, and recent modifications to paste compositions have enabled silver-palladium films to give high bond strengths at elevated temperatures

upon PdSn₃. The formation of this phase is considered to account for the dramatic loss in adhesion when soldered conductors containing palladium are stored at high temperatures.

The purpose of this article is to re-examine silver-palladium conductors from the

materials viewpoint. It is admitted at the outset that the complex nature of this system has not yet allowed a complete understanding of the interactions occurring in solder-coated silver-palladium metallisations. Some of these shortcomings are discussed in greater detail in subsequent sections. It will be demonstrated, however, that, providing certain important chemical aspects of the silver-palladium system are recognised, and appropriate action taken, tin-soldered silver-palladium films may be used with renewed confidence in compact circuitry operating at elevated temperatures.

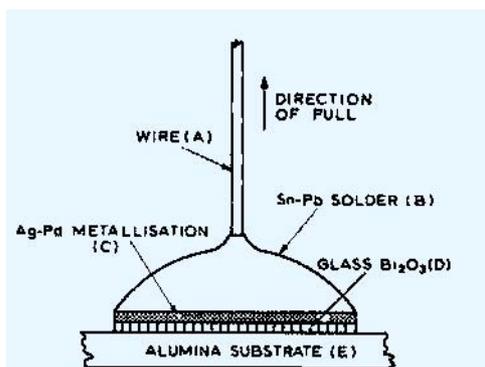


Fig. 1 Simplified cross-section of a soldered silver-palladium film deposited on an alumina substrate

Thick-Film Silver-Palladium Conductors

The system which will be discussed in the following sections may be best considered with reference to Figure 1 showing a simplified cross-section of a soldered assembly. In this assembly the glass and bismuth oxide

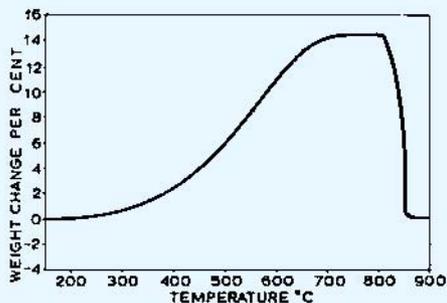


Fig. 2 Thermogravimetric analysis of palladium powder. Heating rate 4°C/min; normal atmosphere

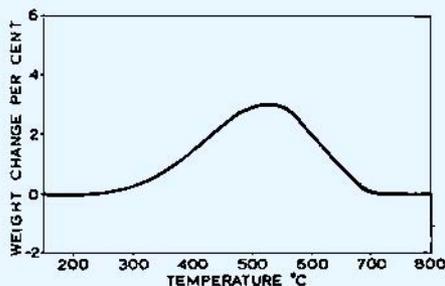


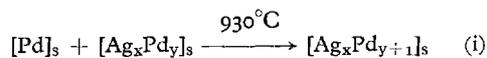
Fig. 3 Thermogravimetric analysis of 69.7 atomic per cent silver-palladium powder mix. Heating rate 4°C/min; normal atmosphere

(layer D) have concentrated at the substrate surface, forming a bond between the ceramic and the silver-palladium layer (C) above. A wire (A) is attached orthogonally to the metal film using a tin-lead solder (B). Of course, under real conditions there has to be a considerable amount of inter-diffusion among these layers in order for the solder assembly to retain integrity. The model shown in Figure 1 will, however, be used as a basis of discussions when reviewing failure modes of soldered silver-palladium conductors under tensile stress.

The Silver-Palladium System

Silver and palladium form a continuous series of face-centred cubic solid solutions displaying a simple phase diagram—a feature expected from the similar electronegativities and atomic radii of the two elements. In

spite of this, however, the two metals alloy with appreciable heats of reaction reaching a maximum of -5.7 kJ g/atom at around 60 atomic per cent silver for the solid reaction:



Integral thermodynamic properties of this system were established by Chan and Hultgren (4) using tin-solution calorimetry. It was noted in the course of their work that the reaction of solid palladium with liquid tin was accompanied by a large negative enthalpy of solution. This behaviour was unexpected not only because of the magnitude of the exothermicity (-109 kJ g/atom; 430°C), but also because silver, with physical similarities to palladium already noted, dissolved endothermically in tin (16.7 kJ g/atom). It appears, therefore, that in the liquid phase at least the formation of palladium-tin intermetallics from the two elements is favoured thermodynamically.

Alloy formation in metallisations containing the parent metals, silver and palladium is complete well below the peak temperature of standard firing schedules (850°C). This is shown both by suitable X-ray investigation and by thermogravimetric analyses (TGA) of the metal powders when heated singly and in combination. Little weight change is observed when silver metal is heated alone under normal atmospheric conditions because of the low stability of Ag_2O (5). On the other hand, thermal analyses of palladium metal when heated under similar conditions showed weight changes as recorded in Fig. 2. The initial weight gain, due to metal oxidation:



is complete at 640°C , and the PdO formed is stable up to 820°C ; beyond this point the oxide is unstable and rapidly reduces to the metal. In the presence of silver, the redox behaviour of palladium is quite different, as can be seen from the thermogram reproduced in Figure 3. Here, under similar oxidising conditions, a mixture containing 69.7 atomic per cent silver-palladium shows two interest-

ing points when compared with the thermogram for palladium. First, in the presence of silver, the oxidation of palladium is incomplete with a discrepancy between theoretical and observed weight gains amounting to 1.5 per cent; and, second, that reduction of PdO, initiated at $\sim 500^{\circ}\text{C}$, is near complete in the presence of silver at 700°C . The latter temperature, considerably lower than that observed for the reverse of reaction (ii) is, of course, a direct result of this reaction being in competition with the alloying mechanism represented by equation (i). Thus, when palladium is alloyed with a less easily oxidised metal such as silver, any oxide formed (PdO) is itself more readily reduced. This is demonstrated by direct comparison of the thermograms shown in Figures 1 and 2 and indicates that alloy formation in an intimate silver/palladium mix is complete substantially by 500°C .

Identification of the reduction temperature for PdO in the presence of silver gave rise to a model intended to offer novel interpretations of phenomena occurring at the glass-metal interface on firing metallised layers. If these ideas are well-founded, they will require a glass with physical characteristics quite different from those used currently in order to improve the mechanical properties of soldered metallisations. These requirements are explored more fully in the following section.

Interplay between Silver-Palladium and Glass-Bismuth Oxide Phases

The major role of the glass and bismuth oxide in metallising compositions is to provide a means of binding the metal layer to ceramic substrates. For this process to be accomplished in an efficient manner it is necessary to ensure that the contact angle between glass and substrate is lower than that between glass and metallisation. In this way the glass is concentrated at the substrate surface which it "wets" efficiently—a process assisted by inclusion of bismuth oxide acting as a fluxing agent. At the same time, the

glass must be allowed to permeate and "key-in" with the lower regions of the metal layer so that the latter is bound physically to the substrate material. That these predominantly physical bonds in silver-palladium metallisations are inherently strong is supported by observations on unaged soldered samples. Here, using conventional silver-palladium compositions, the over-all tensile strengths of soldered assemblies are limited by the strength of alumina substrates, which frequently rupture with increasing load leaving intact the soldered assembly. This generally occurs at around $3\text{--}4\text{ kN/cm}^2$. After thermal ageing these samples, however, bond strengths fall rapidly with time, with the plane of fracture shifting to that between the metallising layer (C in Fig. 1) and the glass layer (D in Fig. 1). Electron probe analyses on both the substrate and corresponding pulled pad have shown (a) that very little metal deposit associated with the metallisation remained on the substrate, and (b) that the substrate retained a very large proportion of the glass phase from the paste composition. Hence, in order to obtain increased strength in thermally aged soldered metallisations it is necessary to fortify bonding between the glass and silver-palladium metal layers. This may be achieved, of course, by increasing the quantity of glass used in metallisations so that a greater degree of interlock is formed between the vitreous and metal phases. Results to be described will show the extent of improvements in tensile strengths gained using this approach.

Yet another way considered capable of increasing the efficiency of physical bonding between these two phases arises from recognition of the redox behaviour of silver-palladium alloys, as discussed above. It is assumed here that in high glass-containing metallisations the efficiency of metal "wetting" is dependent not only on relative contact angles and mobilities of the vitreous components, but also on the extent that the interface between glass and metal remains

free of physical disturbances during standard processing cycles. Incompatibilities will be present in metallisations if the glass is required to form a coherent bond with a material subject to dissociation under normal firing conditions. Such a situation, it is postulated, is likely to occur in silver-palladium metallisations with oxygen from reduction of PdO not allowing as complete bonding as would otherwise be possible. It is conceivable that this reduction process could prise apart the glass and metal layers, creating minute fissures or channels through which metallic diffusion may proceed at a rapid rate. Attempts have been made, therefore, to avoid these incompatibilities as far as possible by selecting a glass with a softening point lying above the temperature for reduction of PdO but below the peak firing temperature of standard processing schedules. In this way, the mobility and "wetting" characteristics of the vitreous component are retarded until after complete reduction of PdO has been accomplished. The glass subsequently softens and wets the reduced alloy, binding the latter to the ceramic substrate. The degree of success that this innovation has achieved in improving high temperature strengths of soldered assemblies is discussed below.

Experimental Procedure and Results

All pastes were produced by sieve-mixing silver, palladium, glass and Bi_2O_3 powders in correct proportions and dispersing the pre-mixed powders in an organic medium by triple-roll-milling. The pastes, containing 80 weight per cent solids with a silver-palladium ratio of 4:1 by weight, were applied to "Alsimag" 614 substrates using a DEK 1200 screen printer. Substrates were cleaned under reflux with trichlorethylene and dried in dust-proof containers before being used for printing. The printed patterns were dried under infra-red and fired in a belt furnace to 850°C under atmospheric conditions. Resistivities of the fired silver-

palladium films were measured on tracks 0.75 mm wide with an aspect ratio of 60 squares. Adhesive strengths of the soldered films were assessed using 1.5 mm square pads to which tinned copper wires (22 swg) having plane butt ends were attached. The wires were attached orthogonally to the substrate using LMP solder (62 Sn-36 Pb-2 Ag). All traces of solder flux were removed from the substrate by rinsing the assembly in boiling 'Arklone K' before placing samples on life-test.

Tensile strengths of soldered assemblies were evaluated using an Instron tensometer with the crosshead speed set at 8×10^{-5} m/s. The wires were pulled in a plane perpendicular to the substrate surface containing the solder assembly ensuring that at all times the wires remained kink-free.

Thermal ageing of the soldered assemblies was carried out in an oven with a fan-assisted circulating atmosphere; the temperature was held within $150 \pm 5^\circ\text{C}$ during test runs. After thermal ageing a number of samples were withdrawn from the test environment at pre-determined times, allowed to cool to room temperature for at least four hours, and the strengths of solder assemblies evaluated as outlined above.

Returning now to earlier comments, it was necessary as a first exercise, to determine the level to which glass has to be incorporated in silver-palladium metallisations before significant improvements are observed in the tensile strengths of soldered and aged samples. Looking at this problem from a slightly different viewpoint, the question may be re-phrased: to what extent may the vitreous component be included in silver-palladium compositions before other as-fired physical and electrical properties of the films become unacceptable?

To provide an answer, a range of silver-palladium compositions was investigated containing varying amounts of glass and Bi_2O_3 . The fired films were assessed both electrically and for the readiness with which these metallisations accepted LMP solder at

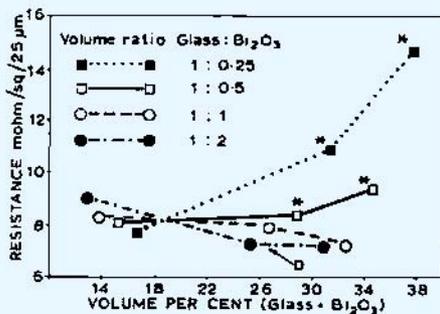


Fig. 4 Resistances of printed and fired silver-palladium compositions as a function of total volume of glass and Bi_2O_3

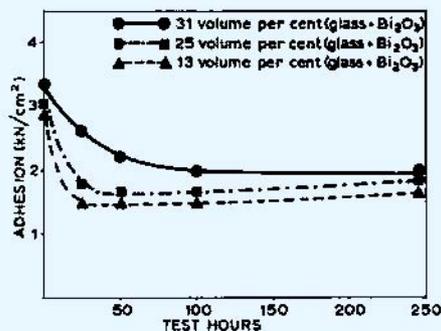


Fig. 5 Life-test adhesion strengths of soldered samples from compositions on curve D (Fig. 4) after storage at 150°C

215°C . Results of these investigations, in which a low softening point ($\sim 450^\circ\text{C}$) borosilicate glass was used in the silver-palladium compositions, are shown in Figure 4. Here electrical data for fired films are plotted against volume contents of the glass and Bi_2O_3 expressed as a percentage of total (volume) content of the solids in the metallisation. Those compositions which yielded films with poor soldering characteristics are marked by an asterisk. Not surprisingly, one of the features to emerge first from Figure 4 is that the quantity of glass which may be included in silver-palladium films and, at the same time, produce acceptable fired electrical results, is dependent on the quantity of Bi_2O_3 with which the vitreous component is associated. Thus, if compositions are required with volume contents of glass and Bi_2O_3 in excess of 20 per cent, and this will be shown to be the case later, then the volume ratios of Bi_2O_3 to glass should not be less than 1:1.

The initial and thermally aged tensile strengths of soldered assemblies using silver-palladium compositions given by curve D of Figure 4 have been evaluated and the results reproduced in Figure 5. Here it is seen that the composition containing ~ 30 volume per cent of glass and Bi_2O_3 yield films which showed the greatest resistance to the degradation of adhesion when stored at elevated

temperatures. Even so, soldered films with around 30 volume per cent of glass and Bi_2O_3 , which represents somewhere near the upper practical limit, display a continuous downward trend in tensile strengths to 100 hours with adhesions levelling off at ~ 2 kN/cm^2 . At this stage, the major fracture mode was identified as again occurring predominantly at the interface between glass and metallisation (layers D and C, respectively in Figure 1), with the substrate retaining only small deposits of metallic phase after the soldered assembly had been tested to destruction.

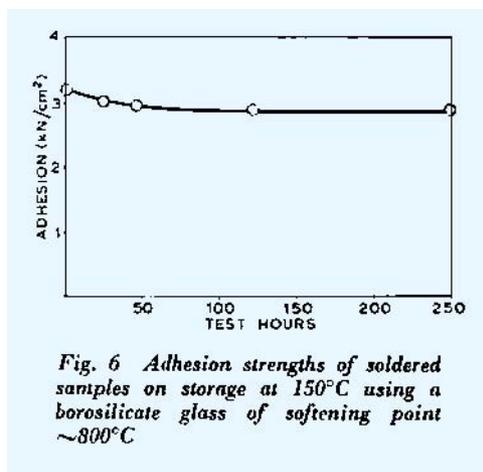
The mode of failure in thermally aged soldered assemblies changes dramatically if the "soft" borosilicate glass used in the metallising composition is replaced by one with a higher softening point. A borosilicate glass was selected having a softening point ($\sim 800^\circ\text{C}$) lying in the quiescent range between the reduction temperature of Ag-PdO and the peak firing temperature (850°C). Using the same volume content of this glass as before (30 volume per cent), silver-palladium metallisations were produced which, after soldering and thermal ageing, yielded over-all tensile strengths shown in Figure 6. The improved adhesions, with mean values at no time during the test run falling below 3 kN/cm^2 , are reflected in a shift in the plane of failure from the glass/

metal interface found with softer glasses to one occurring generally (90 per cent rate) in the metallic deposit (interdiffusion of layers B and C in Figure 1). As a result, after rupturing the soldered joints, a substantial metallic deposit was retained by the substrate. Electron probe studies of these deposits showed that they contained all four metallic elements (Ag, Pd, Pb, Sn) originally present in the metallising composition. The presence of lead could, of course, originate either from the glass or from the solder; no quantitative evaluations have so far been undertaken on these deposits.

Tensile strengths of the remaining 10 per cent of thermally aged samples were limited by substrate "shell-out". This behaviour, also observed in soldered samples which had undergone thermal cycling tests (6), was characterised by the solder joint remaining intact and parting from the substrate with a portion of the latter attached immediately below the joint; a feature quite remarkable in the light of reported tensile strengths of 17.5 kN/cm^2 (7) for as-processed alumina substrates.

Conclusion

It has been demonstrated that if the redox behaviour of silver-palladium alloys is taken into account, then fired metallisations may be obtained which not only readily accept solder but also retain high tensile strengths even after prolonged thermal ageing. This was achieved by selecting a glass with a softening point in the quiescent range between that of the reduction temperature of Ag-PdO and the peak temperature of standard firing processes. In this manner, it is postulated that the glass-metal interface will be subjected to the minimum of physical disturbance and that in the long-term the absence of these local disruptions produces the observed over-all increase in tensile strengths of soldered and aged metallisations. The diffusion rate of the active species has been retarded by ensuring that surface-diffusion mechanisms are minimised and that the



much slower bulk diffusion predominates.

Only limited success was achieved in attempts to identify by diffraction techniques intermetallic formations between lead and tin from the solder and silver and palladium in the metallisation. It has not been possible, so far, to obtain evidence supporting the formation of any well-defined Pd-Sn intermetallic. Furthermore, attempts to identify significant increases in conductor layer thickness after soldering and thermal ageing proved unfruitful. In this context, however, it is worth noting that the formation of voluminous Pd-Sn intermetallics has found some support from studies of soldered, palladium-plated components (8), although in this work the authors conclude that the alloy most likely to be formed (PdSn_2) is not expected to be brittle. As discussed earlier, the observation that palladium dissolved exothermically in liquid tin has to be considered with caution when reviewing the solid-solid reaction between tin (from a lead-tin alloy) and palladium (from a silver-palladium alloy). None the less, such strong chemical attractions would supply the potential necessary for the rapid adhesion degradation found in conventional silver-palladium compositions.

If these attractions play a dominant role, then it is anticipated that the formation of Pd-Sn intermetallics will be accompanied by an over-all contraction in atomic volume, in

keeping with thermodynamic properties of other alloy systems (9). Clearly, more fundamental investigations are required if mechanisms occurring in such complex assemblies are to be better understood. It is through this more complete knowledge that improvements in physical properties of thick-film materials may be presented in a rational form, appreciated and accepted by a market not renowned for its credulity.

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Advances in Platinum-Silver Thick-Film Conductors

Two new series of platinum-silver conductors, described in a recent article by S. J. Stein, C. Huang, L. Chang and G. Schultz of Electro-Science Laboratories, New Jersey (*Solid State Technology*, 1975, 18, 25-33), are intended to supplant palladium-silver compositions in a number of microelectronic applications where traditionally the latter have been considered to offer the most attractive compromise between cost and performance. The electrical and physical performances of six compositions were evaluated; three of these compositions used a vitreous component (fritted systems) to bind the film to alumina substrates, while the remainder (fritless systems) relied upon copper oxides to form a chemical bond with the substrate material on firing. The three compositions belonging to each of the two systems form a series in which the metal ratio of silver to platinum progressively varied up to 2:1.

As anticipated, electrical resistivities of platinum-silver films fired at 930°C increased with platinum content, although films containing equivalent quantities of platinum had near identical electrical properties irrespective of whether the compositions contained glass or not. Similarly, little difference was found in initial peel strengths of soldered samples based on either fritted or fritless platinum-silver compositions. Soldered samples from both the fritted and fritless platinum-silver compositions again showed

no major discrepancies in adhesion values after thermal ageing.

Ultrasonic bonding of aluminium (1 per cent silicon) wire was considered to be more efficient with fritless platinum-silver compositions than with the glass-containing counterparts, presumably because in the former case there is no danger of the vitreous component residing on the conductor surface thereby impeding the bonding operation. Highest platinum content fritless materials appear to show least degradation in adhesion on thermal ageing. On the other hand, fritted platinum-silver pastes appear ideal for thermal compression bonding of gold wires.

Compatibilities of both fritted and fritless platinum-silver conductors were assessed using three dielectric materials and a number of thick-film resistor pastes from three different systems. Fewer compatibility problems were encountered with dielectric materials when glass-containing platinum-silver conductors replaced the fritless electrode materials. All platinum-silver films in the pre-fired form were found to be compatible with resistor pastes from the three systems.

These two platinum-silver thick-film conductor systems thus appear to offer some advantages over conventional, glass containing palladium-silver compositions particularly where the complete absence of oxidation on the surface of films would significantly improve methods of circuit fabrication.