Palladium-Silver Resistor Pastes

AN INVESTIGATION OF FIRING REACTIONS

Thick film circuits produced by screen printing and firing circuit component materials in paste form on refractory non-conducting substrates are widely used in the electronics industry. The electrical properties of the components should be reproducible to within narrow limits, and to achieve this the rheological properties of the pastes and the parameters of the printing process are controlled to standardise deposit thickness. In the case of resistor pastes of the palladium-silver type, comprising palladium, silver and glass frit powders dispersed in organic media, chemical changes occur when the pastes are fired which necessitate rigid control of firing conditions to achieve reproducible results.

Thermogravimetric studies to elucidate the mechanism of reactions occurring in several Du Pont palladium-silver pastes have been carried out by P. H. Krahl and A. F. Bogenschutz, of the Research Institute of Allgemienen Electricitätgesellschaft, AEG-Telefunken, Ulm (*Metall*, 1968, **22**, (10), 988). The authors used powder material for the gravimetric work, obtained by evaporating the liquid constituents from resistor pastes, and printed films for the electrical measurements. The powders were heated in stages to 900°C, and test values obtained by removing samples, cooling and weighing. Resistivities under parallel conditions were determined on printed specimens on alumina substrates.

The results show that a progressive increase in weight and resistivity occurs up to 600°C due to oxidation of palladium, and a reduction in weight and resistivity at higher temperatures due to reduction of palladium oxide. However, neither reaction seems to proceed to completion, nor do weight and resistivity entirely synchronise at above 400°C. Resistivity increases occur, particularly on prolonged heating, with no corresponding increase in weight. Some explanation for these anomalies may be found in the authors' conclusion that protection of some of the palladium and palladium oxide particles by sintering frit retards or inhibits chemical change and reduces electrical continuity. There is little evidence, however, to support the suggestion that palladium oxide assumes a more stoichiometric composition at the higher firing temperatures, or that significant amounts of palladium or palladium oxide dissolve in the zinc borosilicate frit.

No weight changes occur in the silver and frit constituents of the pastes, but silver is shown to have some effect on the palladium reactions. The evidence supports the authors' contention that this is due to a catalytic effect resulting from the formation and immediate decomposition of silver oxide, and not to the formation of a surface palladium-silver alloy as postulated by other workers.

The particle size of the frit is stated to affect the reactions. It seems likely that the particle size of the palladium and silver powders could also have some effect, and in addition that carbon derived from decomposition of the organic paste constituents could be retained in the film at 300° to 400°C long enough to retard the oxidation of palladium, but these possibilities do not seem to have been investigated.

This work has shed some light on the reactions that occur when palladium-silver resistor pastes are fired, although more experimental evidence would be desirable to support some of the conclusions that have been drawn. Because the reactions do not reach completion, it is evident that unless the time and temperature of the firing operation is rigidly controlled, variations will occur in the chemical composition and physical form, and hence the electrical properties, of the resistor elements. F. E. K.