

Thick-film Ruthenium Resistor Pastes

NEW COMPOSITIONS FOR SCREEN-PRINTED CIRCUITS

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New and improved compositions of pastes for ruthenium resistors have been developed at the Johnson Matthey Research Laboratories. Evaluation of the properties of such resistors shows that these materials are suitable both technically and economically for use in circuits designed for the domestic electronics market. This article is based on a paper given at Internecon 72, Brighton, last October.

During the last few years thick-film hybrid microelectronics has evolved into a technology which is being used in circuits of increasing sophistication and complexity. These advanced applications have required thick-film materials with improved electrical properties capable of functioning reliably under conditions that until recently were considered impracticable for hybrid circuits. At the same time, thick-film hybrid modules are being developed for use in equipment designed primarily for the domestic market. Here the main requirements are for inexpensive compositions which, while producing films with satisfactory electrical performances, can be processed easily under conditions which do not have to be controlled stringently to ensure success. These apparently conflicting demands have in this technology nowhere been more problematical than with thick-film resistor compositions.

It was with these diverse roles in mind that a new range of thick-film resistor pastes has been developed at the Johnson Matthey Research Laboratories. This range sets out to satisfy what was considered to be a number of fundamental requirements. First, the resistor compositions should be versatile. This means, among other things, that the inherent electrical properties of the resistors should display minimal dependences on, for example, the shapes and sizes of printed areas and on the

conditions under which these films are processed. Secondly, of course, the pastes should yield, over a wide range, films with high electrical performances—in particular, low temperature coefficient of resistance (TCR), low current noise and good stability in electrical properties when stressed under extreme life-test conditions.

Workers in the Johnson Matthey Research Laboratories had shown earlier that resistor compositions based upon ruthenium dioxide display good electrical properties and produce thick-film resistors acceptable for many applications (1). Ruthenium dioxide, which is stable under normal atmospheric conditions up to 1000°C (2), has electrical properties which are metallic in nature with a resistivity of about 50 $\mu\text{ohm cm}$ and a TCR value of +3000 ppm/deg C (3). The thick-film resistor compositions now developed use a double oxide of niobium and ruthenium together with a glass component suspended in an organic medium. By doping ruthenium dioxide with niobium pentoxide it has been shown that the high positive TCR value intrinsic to ruthenium dioxide may be conveniently attenuated (4).

The glass phase in the resistor paste should be compatible with the conductive species, the the substrate material and a number of different electrode compositions. The glass used is a member of the lead borosilicate family

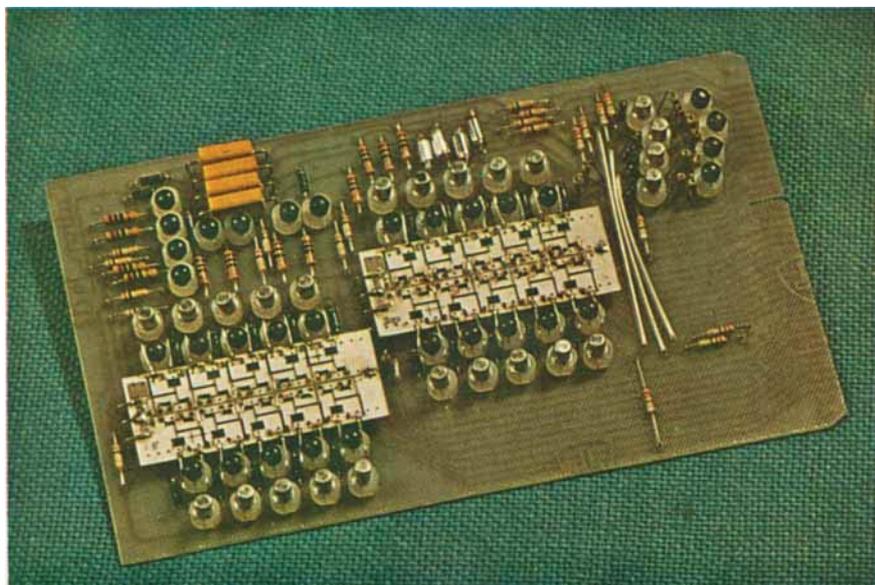


Fig. 1 This decimal counter manufactured by Culton Industries Ltd. includes two sets of 50 ruthenium resistors, which were printed and fired on to $2\frac{1}{2}$ in \times 1 in alumina substrates using Johnson Matthey RF resistor pastes

prepared under carefully controlled conditions to ensure purity and reproducibility.

The two solid components—the ruthenium-niobium oxide and the glass—are mixed

thoroughly by milling before being dispersed in an organic medium. The medium or vehicle imparts the correct rheological or flow properties, making the pastes suitable for

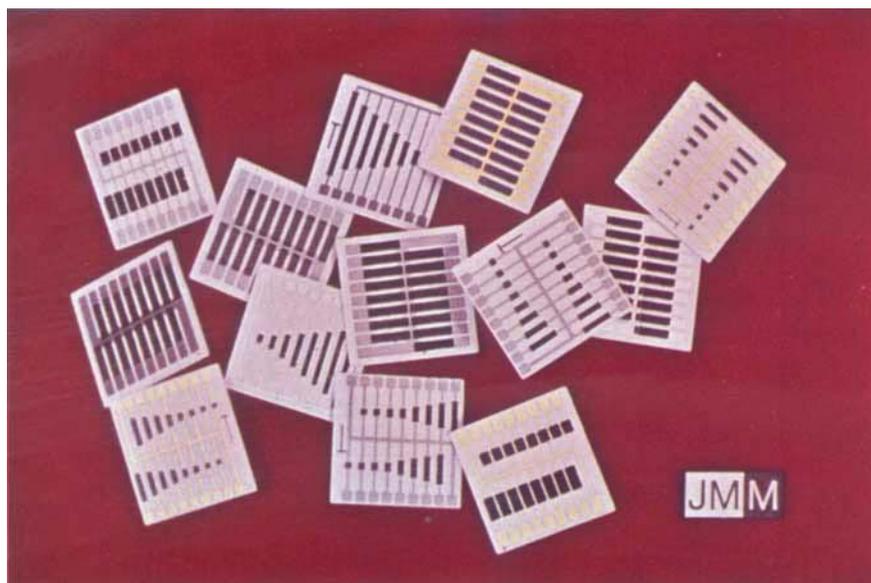


Fig. 2 Test patterns used to assess the basic electrical performances of thick-film ruthenium resistors. The resistor compositions are compatible with a variety of electrode materials, such as gold, gold-palladium, gold-platinum, silver, and silver-palladium

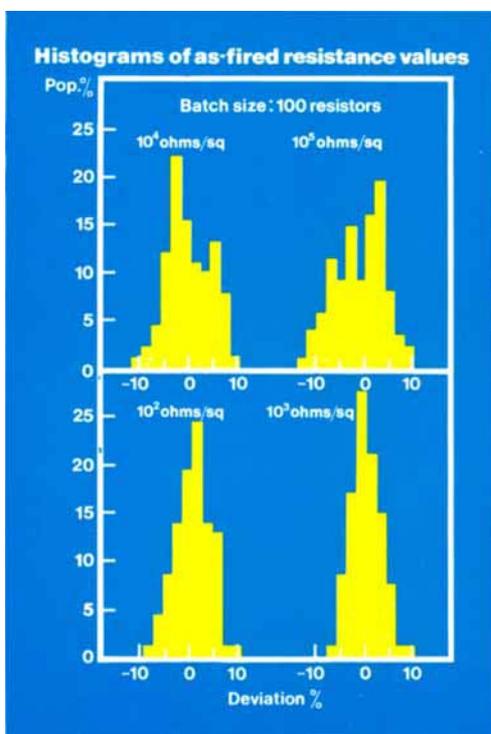


Fig. 3 Reproducibilities of as-fired resistance values for ruthenium resistors. These materials, printed and fired with silver-palladium electrodes, have coefficients of variation of approx. $\pm 3\%$

Assessment of Performance

The performances of thick-film ruthenium resistors have been assessed over a range of printing, firing and life-test conditions. Examples of test patterns used to obtain some of this information are shown in Fig. 2. The electrical properties of the printed and fired films are logged automatically and the results are computed to yield mean sheet resistance, coefficient of variation and also sketch histograms of the results.

The histograms displayed in Fig. 3 are for as-fired resistances of 100 tracks from each of the compositions 10^2 , 10^3 , 10^4 , and 10^5 ohm/sq. Coefficients of variation (standard deviations) less than ± 5 per cent may be obtained readily for resistance values within any one batch over the range 30 ohm to

use in automatic and semi-automatic screen-printing machines. The pastes show no solid precipitation after prolonged storage, and pre-rolling is not required before the materials are used.

After drying the films are fired in a belt furnace programmed to a relatively simple profile having a peak temperature of 760°C . On firing, the conductive species and glass component remain chemically inactive; the important reactions occurring in the films are confined to oxidation of organic constituents from the medium and to fusion of the glass. The thickness of the fired films is between 12 and 15 μm .

Fig. 4 Variation of resistance with peak firing temperature for thick-film ruthenium resistors. The throughput time of the firing process was kept constant and the peak firing temperature was shifted by 10 deg C either side of the recommended 760°C

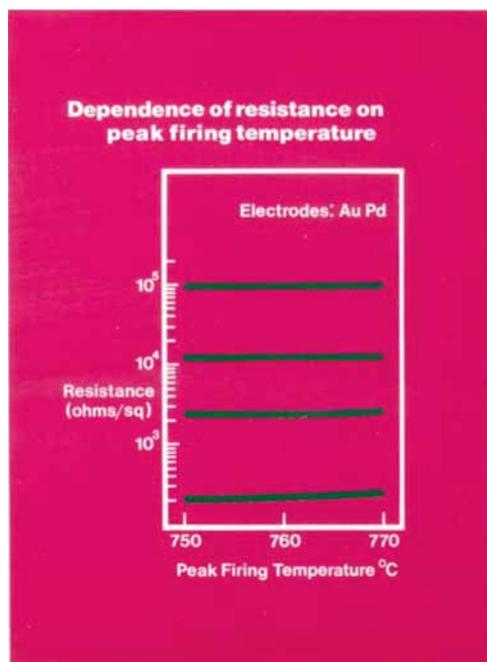
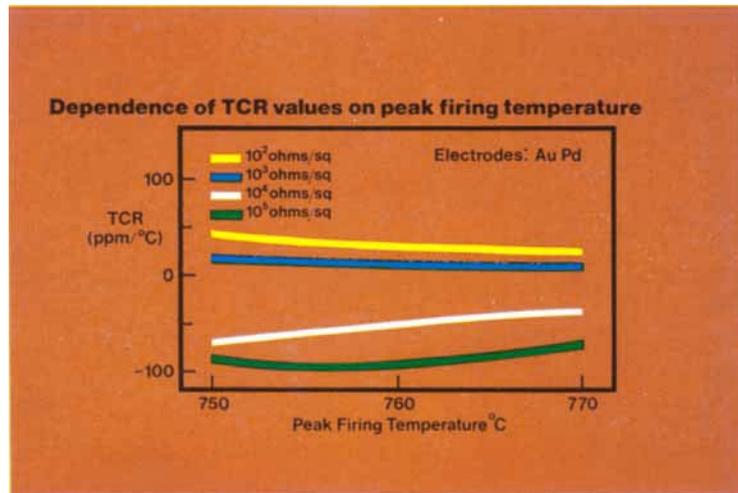


Fig. 5 Variation of temperature coefficient of resistance (TCR) with peak firing temperature for thick-film ruthenium resistors. Firing conditions were identical to those of Fig. 4



10^6 ohm. Similar analytical treatments of TCR values for a given resistor composition show that tracking within 10 ppm/deg C is achieved.

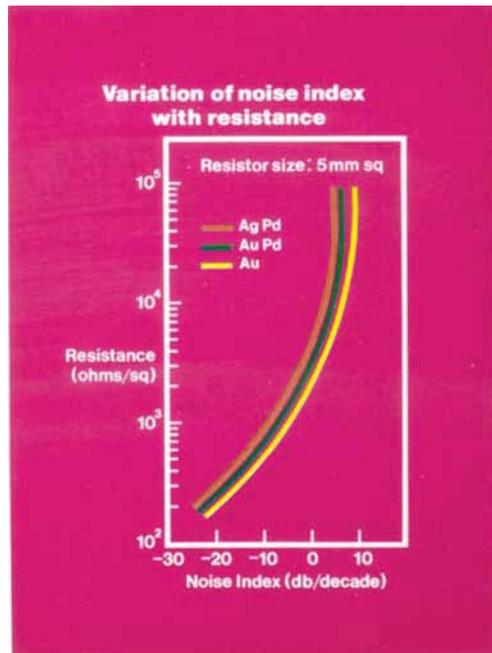
The results in Fig. 3 were obtained for resistor compositions processed on a firing schedule having a peak temperature of 760°C . However, if that firing cycle is now altered, only minor shifts are produced in resistivity levels of the fired films and the reproducibilities of results remain unimpaired, as seen in Fig. 4.

The small changes in resistance with peak firing temperature are accompanied by equal minor shifts in TCR values, as seen in Fig. 5.

These resistor compositions therefore can accommodate quite a large degree of latitude in firing conditions without producing significant changes in the basic electrical properties of the films. Nor is it necessary to limit the shape of resistor track to obtain the intrinsic resistance value for these materials.

Fig. 6 Electrical noise values for 5 mm square ruthenium resistors printed and fired with three different electrode materials. For this resistor size the zero level of db/decade occurs at 3×10^3 ohm/sq

The aspect ratio (i.e. ratio of resistor length to width) can be varied an hundredfold without producing a dramatic change in the inherent electrical properties of a given composition. Some examples of various aspect ratios can be seen among the test patterns shown in Fig. 2. If the aspect ratio is kept constant, the track resistance of a given composition retains a consistent value over a wide range of resistor sizes (5).



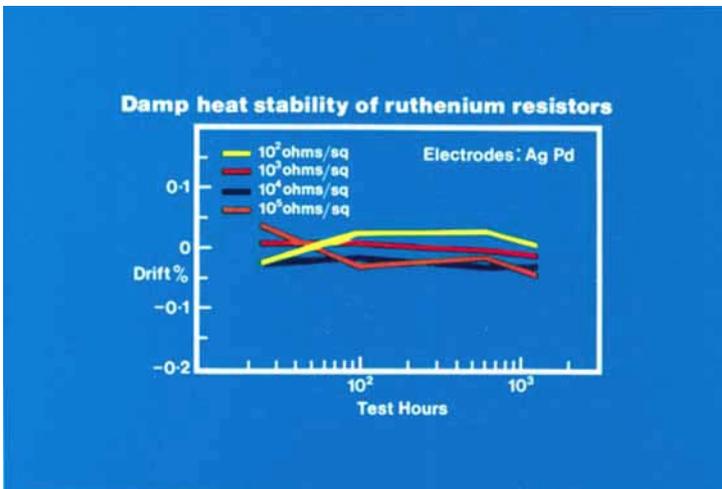


Fig. 7 Damp heat has little effect on the electrical properties of ruthenium resistors. These resistors were printed on to silver-palladium electrodes and remained unencapsulated throughout testing

The electrical noise values of ruthenium resistors are low and display a characteristic dependence upon the size of resistor track (6).

Furthermore, keeping the aspect ratio constant, the noise levels are found to be independent of electrode material, as shown in Fig. 6.

Surface Characteristics

The surface characteristics of fired resistor tracks have been assessed both by profilometer and by scanning electron microscopy. The surfaces of printed and fired ruthenium resistors are smooth, having centre line average (CLA) values of between 0.3 and

1.0 μm . It would seem on this evidence that the surface features make these materials ideal candidates for use in trimmers and in hand-controlled potentiometers. Evaluations of resistor tracks under test conditions employed for potentiometric devices have justified these expectations.

Printed and fired resistor tracks have each been subjected to 400,000 wiper sweeps and in each case the track resistance, track linearity and contact resistance variation (CRV) have been measured before and after testing. Track resistances changed by less than 0.5 per cent from original values, and track linearities retained a constant value

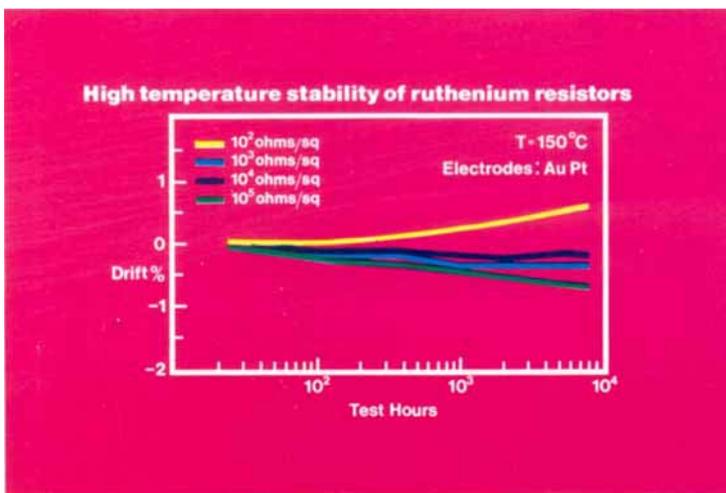
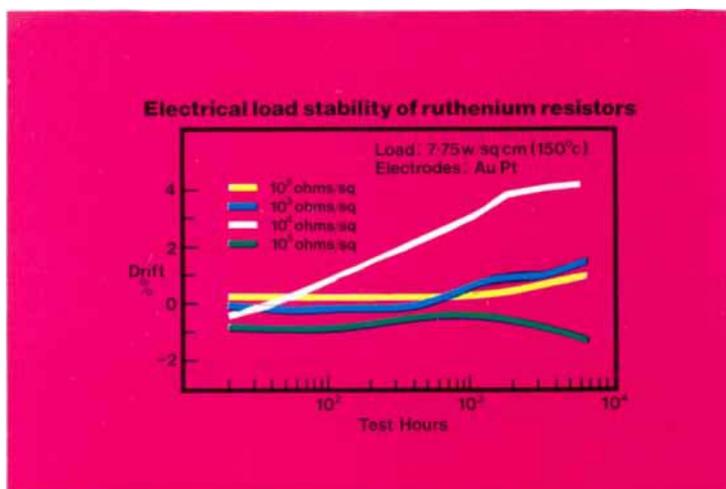


Fig. 8 The electrical properties of ruthenium resistors remain stable when subjected to high temperatures. These resistors were printed on to gold-platinum electrodes and remained unencapsulated during testing

Fig. 9 Performance of ruthenium resistors stressed at 7.75 W/cm^2 d.c. loading and held in an ambient temperature of 70°C . These conditions produced operating temperatures close to 150°C . These resistors were printed on to gold-platinum electrodes and remained unencapsulated throughout testing



throughout the test at around ± 1 per cent. CRV values under these test conditions remained well below 3 per cent of the track resistance.

The bulk properties of ruthenium resistors have been life-tested under both static and dynamic conditions. In the former case, samples were subjected to damp heat and dry heat environments under conditions of no electrical load.

First as shown in Fig. 7, under damp heat conditions, resistance changes are within ± 0.05 per cent of original value after 56 days exposure to 90 per cent relative humidity at 40°C . This meets the conditions outlined in British Standard BS2011: Methods for the Environmental Testing of Electronic Components and Electronic Equipment.

Under dry heat conditions, as shown in Fig. 8, and again with no potential applied to the samples, drifts in resistance values of approximately ± 0.5 per cent are found after nearly 10,000 hours at 150°C .

With a power dissipation in each resistor of 7.75 W/cm^2 (50 W/in^2), the drifts in resistance for these compositions are small—around ± 1 per cent of the original value after a test period approaching 10,000 hours (Fig. 9). Under the d.c. load conditions imposed the high ohmic samples, 10^4 ohm/sq and 10^5 ohm/sq, were exposed to voltages

equivalent to 1000 V/in and 3250 V/in, respectively. It can be seen from Fig. 9 that these materials are capable of operating reliably under conditions of high voltage stress such as are found in, for example, domestic television sets.

Available Compositions

What is therefore available at present is a range of ruthenium resistor compositions having TCR values generally better than ± 100 ppm/deg C; the materials are capable of operating reliably under the severe conditions now employed to test printed and fired components in hybrid circuits. It has also been shown that these resistor pastes may be readily processed under a variety of conditions which little affect the inherent electrical properties of the system.

The adaptability and versatility of these materials have been demonstrated in practice and examples are shown in Figs. 1 and 10.

Figure 1 shows a prototype thick-film decimal counter in which the perforated substrates carry 50 resistors with values from 10^3 ohm to 10^6 ohm, and on the underside 20 thick-film capacitors each of 200 pF. Connections from one surface to the other are made by lead-throughs and form convenient mounting areas for the 30 diodes required by the circuit. The counter is

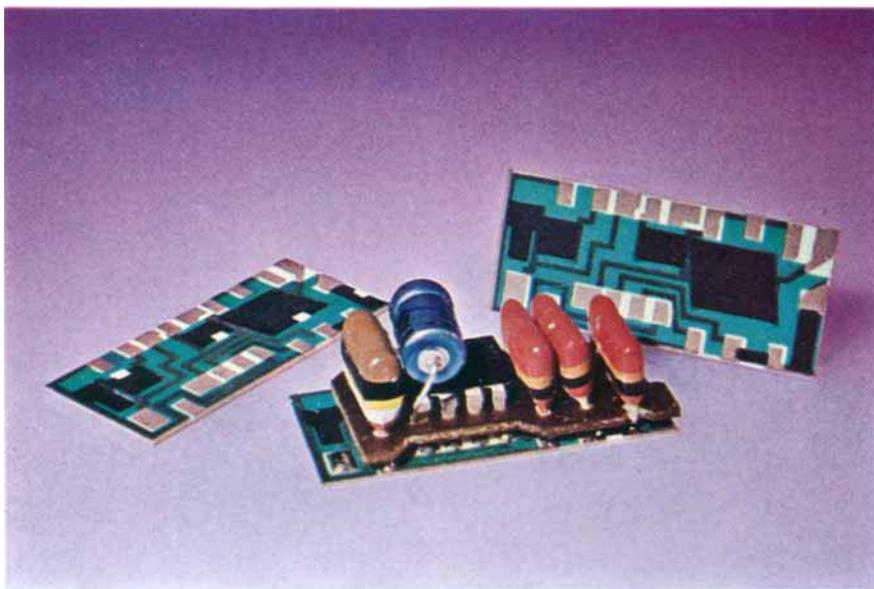


Fig. 10 This circuit using Johnson Matthey thick-film ruthenium resistor compositions was designed by Pye Dynamics for incorporation into an automobile tachometer manufactured by Smiths Industries Ltd. Ruthenium resistors in such an application combine superior electrical performance with low cost

capable of delivering high voltages (75 V) and, by invoking thick-film techniques, the required number of passive components can be accommodated within the available area of the printed circuit board. After fabrication of the thick-film components the diodes were mounted on the underside of the substrates and are not visible in Fig. 1.

Figure 10 shows a thick-film hybrid tachometer circuit designed for use in the automobile industry. The fired resistors here have to withstand 600 volts pulsing at 50 Hz without the electrical properties of the materials being permanently influenced.

Conclusions

In conclusion, therefore, this high-grade thick-film ruthenium resistor system satisfies the advanced requirements of sophisticated hybrid circuits and can be used with economic justification in modules designed primarily for the highly competitive domestic market.

These thick-film ruthenium resistor compositions are at present available over the range 30 ohm/sq to 10^6 ohm/sq. Eventually

these resistor compositions will be developed to cover the full range 1 ohm/sq to 10^7 ohm/sq, thus offering engineers even further flexibility in designing passive thick-film circuits. An extensive evaluation programme is being conducted to establish the response of ruthenium resistors to laser trimming and the effect that this has on the long-term stabilities of these materials. Indeed, the electrical performances of ruthenium resistors are under constant surveillance to meet readily the progressive demands of thick-film hybrid circuit design.

References

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