

A USER MADE THICK FILM SYSTEM†

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This paper describes the state of the art in the development of a polymer based printed circuit board (PCB) compatible resistor ink system. The subject is treated from the standpoint of the manufacturer who, up to now, supplied himself with PCB circuitry.

1. INTRODUCTION

The advent of thick film systems and hybrids inevitably leads to applications where the outstanding technical performance is balanced by an important materials cost. Most paste suppliers counter this trend by developing systems with economical features (non-noble metal conductors, lower and shorter firing profiles, enamelled steel substrates, high speed printing etc.). In general one can say that these developments tend to duplicate the usual cermet characteristics with cheaper processing costs.

In this paper however, we will focus on high volume applications in electronics where these superior cermet specifications are not essential but where the profit margin is small and unflexible. Television-set manufacturing is a good example for such an application. In this kind of electronic circuitry it is quite straightforward to develop a thick film technology compatible with printed circuit board technology.

In doing so, we can easily integrate both discrete and film components on one substrate. Moreover, we can rely on the serigraphic know-how which is available in several printed circuit board manufacturing units.

Up to now this idea was propagated by two kinds of suppliers:

- 1) electronic circuitry subcontractors,^{1,2}
- 2) printed circuit board compatible ink manufacturers.

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In this paper we will take the standpoint of yet another party: the manufacturer of the equipment who, up to now, supplied himself with the printed board circuitry. Apparently he is the one most directly involved with this new development.

2. PROBLEM DESCRIPTION

The technology to be developed should show the following features: use of additive serigraphic processes, ink curable on printed circuit board materials, laser trimmable, compatible with all printed circuit board processing manipulations (e.g. wave soldering, ultrasonic cleaning).

With respect to cermet film technology we probably will have to sacrifice on the performance of the following characteristics: temperature coefficient of resistance, long term stability, power dissipation, current noise.

We further avoid multiple layers and metallised holes. In short, we started the development for film resistors printed on the back side (the copper side) of a single clad, printed circuit board.

Starting from all these assumptions, we made the following options for the development of the paste systems:

- a) binder: two step thermosetting polymer of the same kind as those used in printed circuit board substrates;
- b) conductive agent: carbon.

In the next section, we will deal with some selected research topics for the development of this system.

Out of the great variety of available printed circuit board material, we selected Hp 2062.8

(according to DIN 7735) in 1.5 mm sheet form. We used the same material in the single clad form. It is simply called PC board hereafter.

3. SELECTED RESEARCH TOPICS

3.1. Binder Material

We buy the linearised polymer as a solid, but soluble, material from the specialised supplier. This polymer is produced in large quantities for a number of industrial applications (e.g. injection molding).

In Table I we compare the results for the sheet resistivity (R_{\square}) of three series of our pastes that were processed in the same way. If we compare the first and the second line of Table I, we can see that over a broad R_{\square} range all the sheet resistivity values drop. The only difference between these two series is the batch number of the basic polymer material. If however the viscosity of the polymer solution of the second batch is adjusted to the one of the first batch, the R_{\square} approach their original values.

Gel permeation chromatography (GPC) is an appropriate method to gain more information about the composition of the linear polymer. These GPC curves prove indeed that there are a lot of differences between the two batches. The dispersion factor for batch A is 2.60 and for B 2.89. A more detailed study shows not only a marked difference in the molecular weight distribution on the high polymer side (see Figure 1) but also some striking points on the lower polymer side.

The details in the dimer peak are interesting; indeed it is known that the isomers of this fraction have quite different reaction constants.³ The difference in the monomer peak could be the result of a reaction process divergence that occurred during the production of the batches.

In theory it is possible to infer the molecular mass distribution function from a GPC curve (if a calibration over the entire molecular weight range is available). This study is far from a trivial problem as can be concluded from recent bibliographies.⁴

3.2. Carbon

The first thing to realise is that carbon in an industrial environment appears in two forms: amorphous (carbon black) and crystalline (graphite). The influence of these two carbon morphologies is illustrated by the data in Table II. Obviously the influence on the temperature coefficient of resistance (TCR) is greater than one could expect from the use of the unmixed carbon forms. The optimal ratio however is — as far as TCR is concerned — not a function of the composition alone, because the TCR is also influenced by the substrate material.

Table III gives an example of this phenomenon. In general one can say that the TCR rises with 400 ppm/degree just by switching from alumina to PC board.

Perhaps this is the moment to say something about a resistor model. Although the SEM photographs of a resistor section are not particularly relevant, we will assume that there exists a polymer matrix filled with grains of given mean electrical conductivity. One could guess that the thermal expansivity of this matrix is better matched to PC board (expansivity around $30 \cdot 10^{-6}$) than to alumina (expansivity $8.7 \cdot 10^{-6}$) and thus attribute the substrate effect on the TCR to latent stress in the resistor on alumina after curing. For the morphological effect, one should fall on the difference in temperature behaviour for the mean grain conductivity. Differences in TCR between carbon black and graphite were reported before although in another temperature range.⁵

TABLE I
Influence of binder material on sheet resistivity. The filler composition is constant while the polymer batch and its solution viscosity are parameters. Mean values (m) and standard deviations (s.d.) on R_{\square} are given in kohm for n observations

	n	comp. I		comp. II		comp. III	
		m	s.d.	m	s.d.	m	s.d.
Batch A (6.5 Pa.s)	36	9.4	1.3	112	22	880	193
Batch B (9.0 Pa.s)	24	4.4	1.0	30	21	81	163
Batch C (6.5 Pa.s)	36	8.7	0.9	81	12	500	63

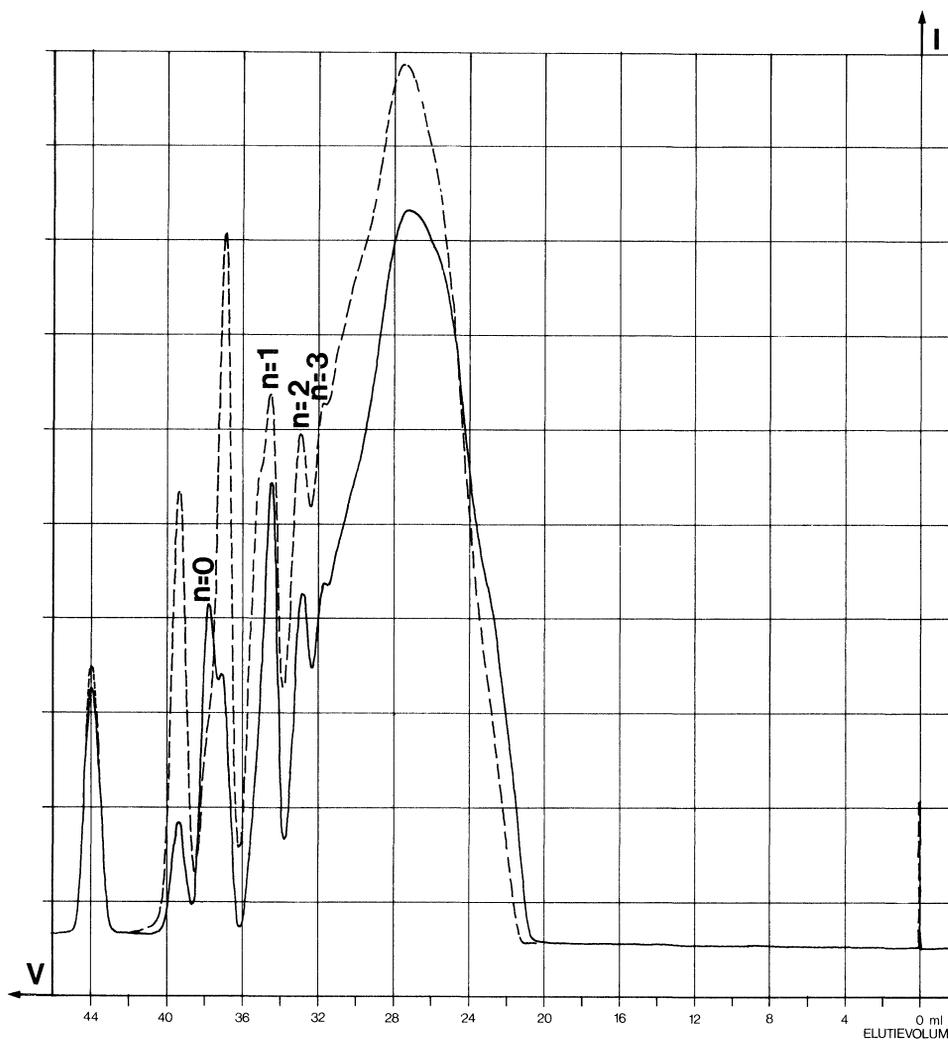


FIGURE 1 GPC for the batches A and B discussed in Section 3.1. The peak height (UV detection) is given as a function of elutionvolume (V). The degree of polymerisation of some fractions is indicated with n.

TABLE II
Influence of carbon morphologies. Some typical values for the sheet resistivity (R_{\square}) and the temperature coefficient of resistance (TCR)

Carbon black/graphite ratio	R_{\square} (kohm)	TCR (ppm/degree) in the 25°C to 75°C interval
100/0	1.22	-390
80/20	1.24	-330
60/40	1.34	-200
40/60	1.02	-150
20/80	0.55	- 40
0/100	0.32	-330

TABLE III
Influence of substrate material. Mean values (m) and standard deviations (s.d.) are given for n observations

	n	Alumina		PC board	
		m	s.d.	m	s.d.
R_{\square} (ohm)	36	1150	90	732	59
TCR (ppm/degree) 25°C–85°C interval	12	–80	25	310	27
relative R_{\square} change for 10% to 90% RH jump	12	6.6%	0.2%	3.3%	0.5%

3.3. Relative Humidity (RH)

Next we consider the sheet resistivity change with the relative humidity. This is illustrated in the third row of Table III.

The effect is rather pronounced in our ink system. The fact that alumina substrates enhance RH sensitivity is a general observation. We suggest that this behaviour has to do with the fact that alumina is less hygroscopic than PC board

At this point we want to make some comments on the mutual influence of TCR and RH sensitivity. From an industrial standpoint one can live with this phenomenon and eventually consider a worst case treatment, but from a research standpoint it is better to split both effects.

Our unloaded drift measurements (not presented here) showed an unexplained fluctuation until we realised that we were measuring the environmental humidity situation.

As a matter of illustration of the effect under discussion consider the following TCR measurements in the 25°C to 75°C interval for resistors of the same run ($R_{\square} \approx 500$ ohm):

- 1) TCR = –290 ppm/degree for a resistor encapsulated in a TO5 package under N_2 atmosphere.
- 2) TCR = –100 ppm/degree for a resistor manipulated in the same way as above but exposed to atmospheric air.
- 3) TCR = 240 ppm/degree for the usual measurement.

We conclude that it is necessary to take special precautions if the temperature coefficient of resistance and not some sort of climatic coefficient of resistance is under investigation. We further suggest that the IEC 115/1 prescription is perhaps not the best way to do the TCR measurement for this type of uncoated film resistors (24 hours drying at 55°C will not help that much if moisture condensates on the resistance at the first measurement on a lower temperature).

3.4. Rheology

In Section 3.1. we have already mentioned an important aspect of the systems rheology: the viscosity of the polymer solution. Figure 2 gives an example of the ink viscosity as a function of shear stress.

The ultimate test for the rheology however, is simply good screening and levelling. We experienced that, in general, it is good practice to use thixotropic additives. Unlike the cermet pastes, we can forget about additives that disappear under curing. So we have chosen a chemical inert additive also used in the paint industry. It is simply SiO_2 with a great specific surface. This product helps to solve screening problems (e.g. small bubble generation after printing). For a given composition there is however an upper limit to the amount of this particular additive. Above this threshold craterlike eruptions occur during the cure process.

An example for thixotropic behaviour is given in Figure 3. Viscosity and thixotropy were measured according to Heinz *et al.*⁹

3.5. Curing

In this section we compare two curing methods: thermal curing (boxoven) and infrared (IR) curing. An infrared absorption spectrum of PC board material shows a minimum in the 2000 cm^{-1} to 1800 cm^{-1} region while the wet spectrum is flat.⁶ So we have done all our IR curing with a 5 micron lamp assuming that the PC board is maximal transparent for this wavelengths.

We also considered another parameter: the heat up velocity. The first two rows of Table IV give the results. In this table slow heat up for thermal curing means oven stabilisation at the curing temperature after insertion of the wet resistors while fast heat up means stabilisation before the resistors are inserted. For IR curing slow heat up is approximately 15 degrees per minute while fast heat up means some

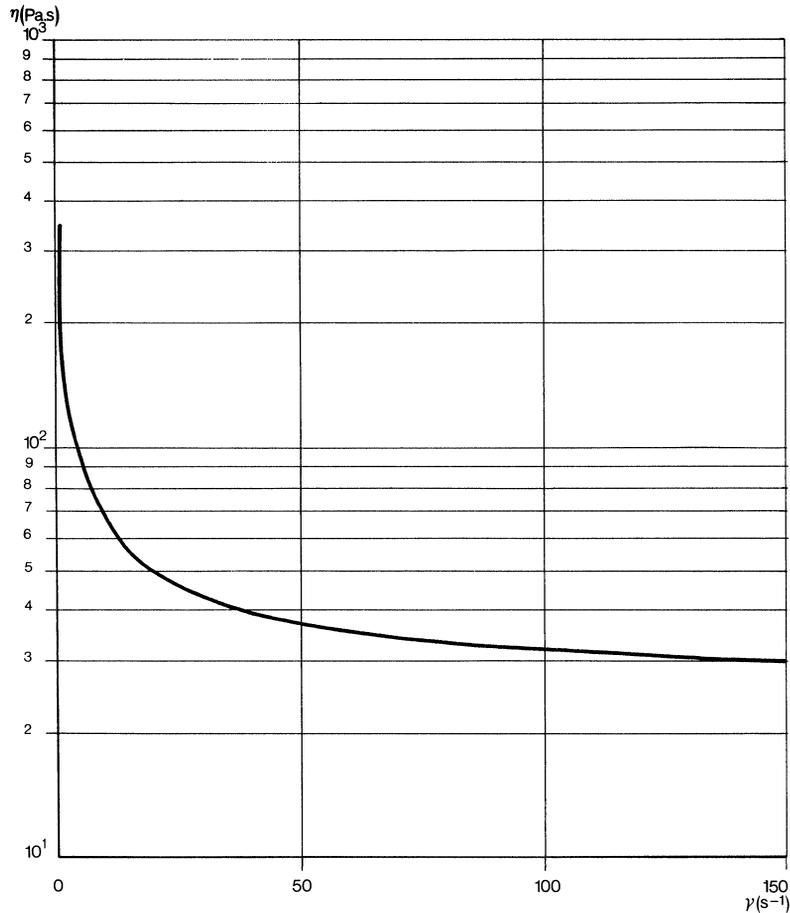


FIGURE 2 Example of a viscosity (η) versus shear rate (γ) plot for one of our pastes.

45 degrees per minute. The latter data were derived from a temperature profile of the stabilised oven. To obtain the data in the third row of Table IV, we repeated the IR cure on samples with a longer cure time (= time at maximum temperature). From the first two experiments one could conclude that a fast heat up is better from a point of view of spread in the final product. The third experiment however indicates that this difference disappears after extended curing.

There remains of course an enormous point in favor of IR curing: the curing time is at least 5 times shorter.

Coming back to our resistor model mentioned in Section 3.2, we can try to understand these results. If the heat up time is slow the three dimensional polymerisation process starts slower (less cross links per unit time for a given chain length) and the filler

material gets a chance to cluster. Consequently there is a bigger spread in grain size and thus in resistor values. Continued curing eventually splits up these bigger clusters into smaller grains of a more comparable size.

The lowering of R_{\square} as a function of curing time is a well known effect in cermet technology.

3.6 Thermal Shock

In this section we concentrate on the effect of wave soldering on PCB compatible resistors screened at the bottom of the board. Table V shows the influence of this kind of thermal shock on TCR and RH sensitivity (relative change in R_{\square} if the RH changes from 10% to 90%).

For the influence on R_{\square} it is possible to perform a correlated test. It turns out that for an $R_{\square} \approx 10\text{kohm}$

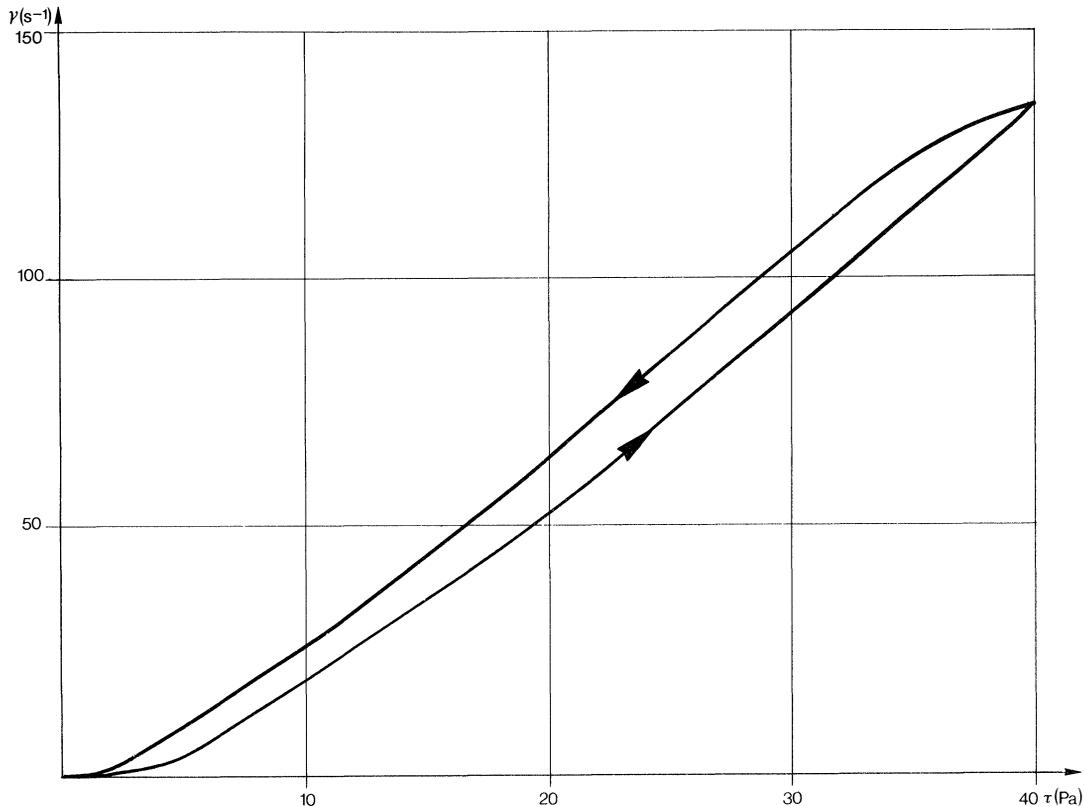


FIGURE 3 Thixotropic behaviour of the same paste as in Figure 2 with shear rate (γ) as a function of shear stress (τ).

TABLE IV
Influence of curing method and cure time. R_{\square} values (in ohm) for the mean (m) and standard deviation (s.d.) for n observations

	n	Fast heat up		Slow heat up	
		m	s.d.	m	s.d.
Thermal cure	108	905	45	1178	82
IR cure (10 min)	72	928	54	1328	194
IR cure (20 min)	120	752	38	867	38

this relative change in R_{\square} has a mean value of 0.9% with a standard deviation of 3.4% for 36 observations.

We have other data that confirm this trend. During the wave soldering process the sheet resistivity of the unprotected resistor screened at the bottom of the PC board will increase, the TCR will lower somewhat and the RH sensitivity becomes slightly worse. However, the results reported in this section were only obtained after thorough preheating before the thermal shock was applied.

TABLE V
Influence of thermal shock on TCR and RH sensitivity. Mean values (m) and standard deviations (s.d.) are given for n observations

	Before m	(n = 12) s.d.	After m	(n = 8) s.d.
TCR (ppm/degree) 25°C–85°C interval	540	100	410	100
Relative R_{\square} change for 10% to 90% RH jump	4.9%	1.5%	5.5%	1.8%

4. FURTHER RESEARCH

Further research should be directed towards the development of the very simple model put forward in Section 3. We need to know more about the structure of the resistor and of the intermediate stages.

The results reported for GPC give a first indication on how to proceed. In a first approach one could try to correlate the dispersion factor with the characteristics of the finished product. Clearly the molecular distribution function of the linear polymer has a relationship with the final matrix structure (if it exists) in the resistor.

There are methods available to gain information on what happens during the curing process.⁷ As an example we give here a differential scanning calorimetry (DSC) plot of one of our inks. In DSC one measures continuously the heat capacity of a sample as a function of a programmable heating cycle. If this heating cycle is linear in time the DSC is a straight line; it can be modulated by positive or negative deviations if exothermic and endothermic processes respectively take place. In more sophisticated studies one can use this heating rate as a parameter to derive the most favorable curing time, or simulate a real cure process by making full use of the programming function. The latter simulation is of

course only valid if the heating agent is the same as in the real process.

In our example (Figure 4) we detect an exothermic and an endothermic process which both practically disappear when the sample is rerun after cooling down. The exotherm is the polymerisation reaction.

The endotherm however could be a simple evaporation of solvent material. The latter conjecture could be checked by a thermogravimetric analysis. The intriguing point is that the evaporation occurs after polymerisation; this could indicate that there exist solvent inclusions in the resistor.

To learn more about the structure of the final product, we can use noise measurements. Two samples of the same run were given a different preheating treatment before they experienced the same thermal shock. The results are given in Table VI.

From the data in the last two columns of Table VI we can calculate β from

$$(R_{\square 1}/R_{\square 2})^{\beta} = (C_1/C_2)$$

resulting in $\beta = 2.1$. In the Vandamme picture of noise⁸ in film resistors this would indicate an intermediate stage between constriction and interface dominated grain conductivity. These results are only given as an example. It would for instance be more relevant to compare 1/f noise data of the same sample before and after thermal shock. These data are not available to date.

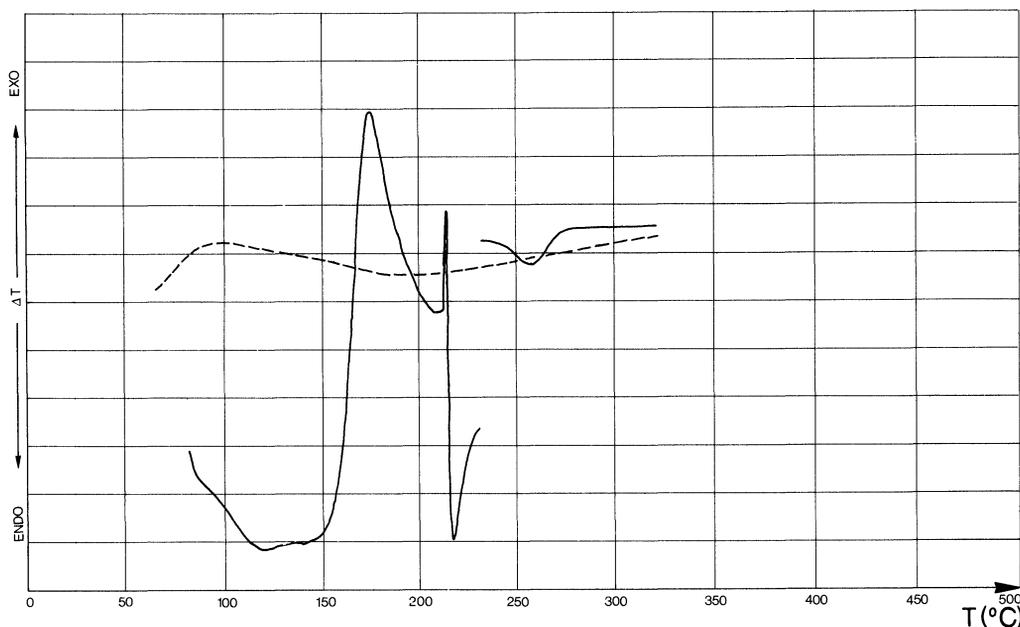


FIGURE 4 An example of DSC plot for one of our inks. Sample temperature is given in the abscissa in °C. The meaning of the ordinate is explained in Section 4. Heating rate was 20°C/min under N₂ atmosphere. The broken line is a plot for the same sample after the first experiment (full curve) was finished.

TABLE VI
Sheet resistivity and current noise as a function of thermal shock. R_{\square} values are in ohms; C is the relative $1/f$ noise intensity

	R_{\square} before preheating	R_{\square} before thermal shock	R_{\square} after thermal shock	C
Sample I	692	706	694	$0.12 \cdot 10^{-1.2}$
Sample II	723	723	1323	$0.50 \cdot 10^{-1.2}$

5. EXAMPLE

In order to assess the possibilities of this technology in a less theoretical way we produced prototypes of an existing audio module for colour TV in this alternative technology.

In this design 26 resistors were produced with three different pastes. They were IR cured and laser trimmed. The remaining discrete elements were hand soldered.

We launched a reliability program on a set of 10 modules in an ambient of 50°C at 90% RH producing maximal power ($6.5 W_{\text{eff}}$). From a quality standpoint there were some noise problems at minimal volume. The problem is located at two specific resistors in the first stage of the amplifier circuit. This impairment can be solved by using discrete components in this part of the circuit. We could however try to solve it from a technological standpoint: either by increasing the surface of this resistance or using conducting additives.

6. CONCLUSIONS

The development of a PCB compatible thick film resistor system is not entirely finished but we think that the prospects are good. In order to develop a consistent resistor model a strong multidisciplinary cooperation is necessary.

From an industrial standpoint we conclude that:

1) this kind of technology has a chance only if the user has a thorough understanding of the ink production and stabilisation process.

2) an apparatus manufacturer with a flexible and diversified product range should be his own principal ink supplier.

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