

THE INFLUENCE OF CONTAMINANTS DURING THE FIRING OF INKS

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During firing of resistor materials the resistance is influenced by gaseous contaminants and by compounds given off by other pastes. Nearly all inorganic salts which are slightly volatile at the firing temperature, and some rather stable organic materials influence the resistor properties. Halogenated materials are the most important and the higher ohmic series the most sensitive.

For aluminium conductors a very high sensitivity to fluorinated and chlorinated compounds has been found but in this case organic compounds have no influence.

1. INTRODUCTION

The fired resistor properties of thick film resistors and conductors are influenced by process parameters, such as the time/temperature relationship of the furnace and by contaminants, which are present during firing in the furnace or which are absorbed before firing starts.

In this last case really large deviations from normal values can arise, even such that the whole batch falls outside the specifications, being in our case a limit of about $\pm 25\%$. The higher ohmic resistors are most sensitive to these kind of materials.

In general this subject has not been dealt with in the literature. Lynch¹ has done a critical study on thick film resistors, in which he determined the influence of the quality of the compressed air in the furnace.

Next to that it is generally known that halogenated hydrocarbons can have a detrimental effect. Only Dupont² has given some figures. They found an influence of only 100 ppm trichloroethylene and of more than 1000 ppm trichloroethane on their 1300 series resistors, while thinners had only a minor influence.

In our factory a large influence of only small amounts (some ppm) Freon TF in the atmosphere on all resistor pastes and on aluminium paste has been found.

Next to these air contaminants it is possible that chemical decomposition products influence the properties of other pastes. For instance it was found that some dielectric and glass pastes changed the properties of cofired resistors, more especially if relative large amounts of these pastes are present in the furnace.

In order to be informed which compounds are responsible for this influence a test has been set up. The emphasis was laid on those constituents which are transported through the gaseous phase but originate from other substrates. As vehicles we used some resistor and aluminium pastes primarily.

2. EXPERIMENTAL DESIGN

A batch of numbered substrates were printed in a reproducible way on an automatic de Haert printer and each tenth substrate was fired in random sequence in a belt furnace at 850°C. The resistance of each resistor was measured and the mean and variation coeffi-

cient calculated for the whole series. In this manner the nominal value of each other substrate is known and a test sample which deviated more than 10% from the mean was considered as influenced.

For the execution of the tests the furnace was stabilized by sending through clean substrates. On one substrate a known amount of the material under test was applied and this one was preceded by 1 and followed by 1 to 20 test samples (Figure 1) and fired. For the application of small amounts of substance (< 10 mg) on a resistor a micro-dispenser with a solution of known concentration was used. After firing the resistance – and sometimes the HTCR – of each resistor was measured.

In order to get an insight into the quantities which affect only one resistor, a known amount of substance – as solution – was applied on a dried resistor and fired in the standard manner.

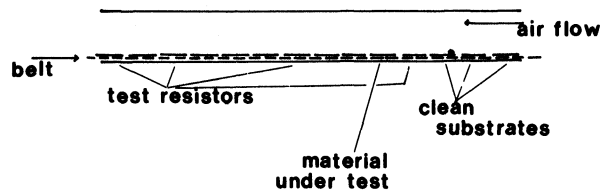
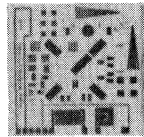
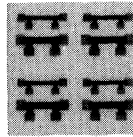


FIGURE 1 Sequence of substrates during firing.

TEST CIRCUITS



AL paste



R paste

FIGURE 2 Testpatterns used.

3. TEST CONDITIONS

3.1 Pastes:

Al paste	Engelhard T 1486
	Engelhard T 2848
	Demetron 67900026
	Demetron 67900008
R paste	DP 1361
	DP 1341
	DP 1321
	ESL 2914

3.2 Pattern:

see Figure 2.

3.3 Printer Settings:

de Haert printer
 Pressure 5–6 N/cm
 Speed 10 cm/s
 Squeegee 65° Sh, under 45°
 Stainless steel screens, 200 mesh.

3.4 Drying:

15 min. at 120°C.

3.5 Firing:

Watkins and Johnson furnace, 4 inch, 50 min. profile with 8 min. dwell time at 850°C.

3.6 Measuring:

Resistance with Philips Digital r.m.s. multimeter PM 2526.

4. RESULTS

With our vapour phase tests in general only a small influence was detected on the sample just *before* the substrate with the material under test and a decreasing influence on those after it, which gave us the indication that the stream of air was definitely in the reverse direction of the belt.

From Table I and Figure 3 it is clear that the resistance value of an unknown sample

TABLE I
 Reproducibility of printing resistors (DP 1361) in one series.

	R 1	R 2
n =	21	21
\bar{x} =	4,44 M Ω	10,55 M Ω
σ =	0,21 M Ω	0,48 M Ω
C.V. =	4,6 %	4,6 %

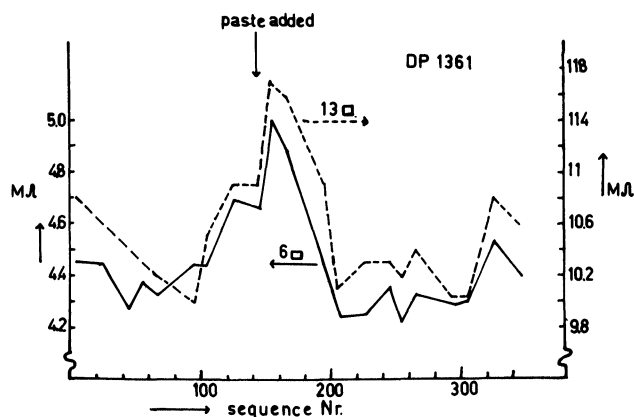


FIGURE 3 Resistance of printed substrates in dependence of sequence.

TABLE II
The influence of 20 μg salt on DP 1341 (applied as solution on a resistor)

Salt	R%	Salt	R%	Acid	R%
KF	-20	Na_2SO_4	-30	HF	<5
NaF	-30	$\text{Na}_2\text{S}_2\text{O}_3$	-30	HAc	<5
KCl	-20	NaNO_3	-35	HNO_3	<5
NaCl	-15	Na_2CO_3	-40	H_2SO_4	- 10
KI	-30			H_3PO_4	+ 10

within a series of printed substrates can be predicted within 5%. As a limit for considering an effect as a positive one a change 10% compared with the reference was taken.

A survey of the qualitative and quantitative results with the R pastes is given in Tables II to VIII and those concerning the aluminium pastes are found in Table VIII.

5. DISCUSSION OF THE RESULTS

From Table II we can see that cofiring of only 20 μg inorganic material on a resistor (of 2-3 mg) leads to a decrease of the resistance by 20-40%. So an addition of only 0.5-5% of the weight of the resistive material can give considerable change in resistivity. Which material has been added is not very important: each one gives about the same change. The addition of a conducting material only brings forward this effect. Some acids have no influence because they are volatilized before reaction can take place.

Those gaseous phase experiments which have given an effect on the 4 resistive materials used are given in Table III. In all, these cases 5 mg of inorganic material was used, part of it being still present after the firing cycle.

TABLE III
The influence of 5 mg salt applied on a separate substrate

Contaminant	DP 1361	DP 1341	DP 1321	ESL 2914
KF	+++	++	+	+++
BiF_3	++			
NH_4Cl	+++	++		
NaCl	+++	+++	+	++
KCl	+++	+++	+	+
NiCl_2	+++	+++		
ZnCl_2	+++			
BaCl_2	++	++		
KBr	+++	+++	+	0
KI	+++	+++	+	+
MoO_3	+++	+++		
Sn/InOx	++			
H_2SO_4	+++	+++	0	0
H_3PO_4		+++		
NaOH	+++	++	0	+++

- * means change positive
- 0 means influence <5%
- + means influence 5-10%
- ++ means influence 10-25%
- +++ means influence >25%

An effect can only be expected if the material can be transported via the gaseous phase in the critical temperature range. Indeed no effect could be observed with very volatile materials, such as HF, HCl and HNO₃ or with substances which have a negligible vapour pressure at 850°C, such as many oxides (CdO, B₂O₃, PbO) carbonates (Na₂CO₃, CaCO₃), fluorides (LiF, BaF₂) and sulfates (Na₂SO₄).

From Table III and IV, it can be seen that, within one series of pastes the greatest effects occur with the higher ohmic ones. Next to that ESL 2914, based on lead ruthenate, differs much from DP 1341, based on bismuthruthenate. If the quantity of inorganic material (Table IV) is under a certain threshold (which is for KCl 0,5 mg) no effect is observed, but above that threshold an exponential increase can be seen.

Cofiring other pastes has no large influence, as should be expected, but DP 9061 and DP 5217 have a significant effect. However if many substrates, each with a harmless amount of paste are present in the furnace, effects will be distinguishable with many pastes.

From Table V the effect of the vapour pressure can be seen. Some halogenides which

TABLE IV
The quantitative influence of some inorganic materials and pastes on resistor pastes

Contaminant		DP 1361	DP 1341	DP 1321	ESL 2914
NaF	5 mg	- 2%	+ 6%	0%	+ 2%
KF		-55%	-24%	+ 11%	+20%
NaCl		-82%	-62%	- 6%	-16%
KCl		-97%	-48%	- 4%	- 6%
KBr		-53%	-36%	- 4%	+ 2%
KI		-44%	-29%	+ 6%	+ 8%
DP 9061	1000 mg	-10%	- 7%	- 4%	0%
DP 9911		- 5%	- 5%	-10%	- 5%
DP 5217		-14%	- 5%	+ 5%	+11%
DP 9101		+ 2%	+ 3%	- 8%	- 3%
DP 8190		- 4%	+ 2%		- 6%
DP 9950		+ 3%	- 8%	-12%	- 6%
DP 8315		+ 4%	- 6%		
DP 1361		- 3%	0%	- 2%	- 3%
KCl	0,1 mg	+ 2%	+ 2%	- 1%	0%
KCl	0,2 mg	0%	- 1%	- 1%	1%
KCl	0,5 mg	- 3%	- 6%	- 4%	1%
KCl	1 mg	-44%	-30%	- 2%	1%
KCl	5 mg	-97%	-48%	- 4%	- 5%

TABLE V
The effect of some salts on DP 1341. The decrease of the resistance value is determined by the vapour pressure of the substance at 850°C.

Salt	20 µg (drop) %	5 mg (vapour) %	vapour pressure mg Hg
NaF	-30	<5	<0,02
NaCl	-15	-60	0,8
NaOH	-	-20	5,4
KF	-20	-20	0,6
KCl	-20	-45	1,7
KBr	-	-36	2,6
KI	-30	-29	5,8

TABLE VI
Organic compounds which influence the resistance value

No effect	Effective
volatile solvents	acetates
terpineol	stearic acid and salts
phthalate esters	soya lecithin
carbon	soya bean oil
ethylcellulose	paraffin wax
polyethylene	bees wax
polyvinylchloride	polyvinylacetate
prinar	teflon

TABLE VII
Effect of the amount of soya lecithin (vapour phase)

	DP 1361	DP 1341	DP 1321	ESL 2914
10 mg	- 7%	-11%	-17%	- 11%
20 mg	-17%	-18%	-19%	- 15%
50 mg	-16%	-21%	-27%	- 18%
100 mg	-22%	-26%	-29%	+ 128%

show the same change, when dosed as drop, show a different effect in the vapour phase primarily on basis of their vapour pressure.

Organic compounds too can influence the resistance value (Table VI). In general, high molecular weight substances, which decompose above 200–300°C and whose decomposition products contain reducing substances, are effective.

The mechanism however is different (Table VII).

In this case the effect depends not very much on the quantities and besides that the influences on the investigated pastes are comparable. The value of + 128% on ESL paste is unexplained.

As pastes contain relatively much organic materials, these are perhaps the most important.

If through some organic or inorganic material the resistivity changes, the TCR is changed too.

The results obtained with Al pastes have been gathered in Table VIII, from which can be seen that the sensitivity to Na/KF or Na/KCl is very large. Here resistivity increases a factor 10^6 .

From Figure 4 it can be seen that even 0, 2 mg NaF has a significant effect and with higher quantities the change is larger and visible over a larger distance in the furnace. With 4 mg NaF, substrates, 100 cm further on are already influenced. If a drop of solution is put on the printed line and fired, only 2 µg of NaF or 10 µg NaCl, being 0,01–0,1% of the metal, gave an infinite resistance with T 1486. The other pastes are somewhat less sensitive, but 10 µg of NaF gave in all cases infinite resistance.

In general T 1486 is somewhat more sensitive to all inorganic materials. This sensitivity, primarily to halogenated substances, can be explained by a change in structure of the metallization. If a contamination is present, the molten drops of aluminium flow together, presumably under the influence of the change in surface tension of the glass, to larger drops, which are expelled from the layer and are visible after cooling down. By this growth in drop size the contact resistance increases, leading even to loss of mutual contact.

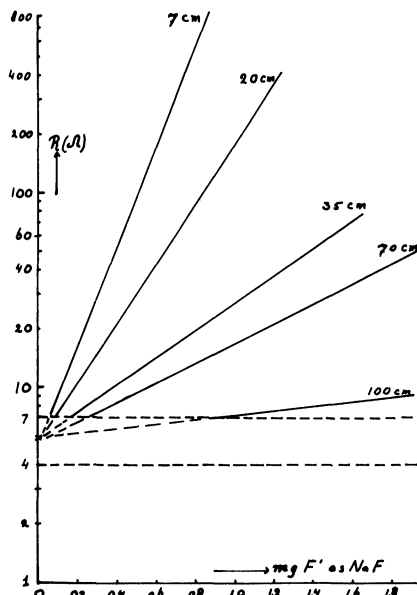


FIGURE 4 Influence of NaF on the resistance of Al pastes.

It is clear that these kinds of pastes are very sensitive to contamination of the furnace atmosphere by halogenated hydrocarbons.

No influence could be detected from organic materials, mentioned in Table VI, or from other pastes, except from DP 5217 (R_{∞}) which contains a fluoride. Even a layer of fired DP 5217 gives infinite resistances with Al pastes.

TABLE VIII
The effect of 5 mg salt (vapour phase) on the resistivity of aluminium pastes (in Ω).

	T 1486	Engelhard T 2848	67900008	Demetron 67900026
reference	4	5	5	3
LiF	35	33	∞	6
KF	∞	∞	∞	∞
NaF	∞	∞	∞	∞
BaF ₂	6	10	5	4
KCl	∞	8	∞	∞
NaCl	∞	5	∞	∞
BaCl ₂	4	8	5	3
NiCl ₂	5	—	∞	—
KBr	16	7	9	7
KI	7	4	7	3
Na ₂ SO ₄	4	4	4	5
Na ₂ S ₂ O ₃	∞	—	∞	—
H ₂ SO ₄	81	4	5	30
NaOH	4	6	5	3
DP 5217	∞	∞	∞	∞

∞ means $> 20 \text{ M}\Omega$.

6. CONCLUSIONS

It has been proven that inorganic materials (salts) do influence the resistive value and TCR of resistor pastes during cofiring, if these compounds are slightly volatile at 850°C. An estimated vapour pressure of 0,01 mm Hg is enough. This is the case for many halogenated compounds. The mechanism of interaction is presumably the adsorption of conducting material, by which the resistivity decreases, and so the higher ohmic pastes are the most sensitive.

Some higher molecular weight organic compounds show the same effect, however in this case a superficial reduction of RuO₂ is more acceptable. All pastes, independent of sheet resistance and composition, show about the same sensitivity. As organic compounds are present in all pastes, this material in general will give the largest contribution. And among them soya lecithin is a prominent one.

Aluminium pastes are very sensitive to even µg quantities of fluorides and chlorides, by which the surface tension equilibrium is changed, forming larger drops of Al, loosening their mutual contact. If the resistivity is of prime importance all such contaminations must be excluded.

Next to these contaminations given off by pastes, a pollution of the furnace atmosphere with organic compounds, containing a halogen, phosphorus, or sulfur atom will undoubtedly lead to resistivity and TCR influences.

REFERENCES

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