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COMPARATIVE STUDY OF THICK FILM DIELECTRICS

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SEM-observation and analysis provide a quick and reliable method of predicting the cross-over and multilayer characteristics of a dielectric paste. Surface and bulk porosity, flow behaviour and chemical composition, determined by SEM are closely related to the results of electrical and environmental tests. From the latter, voltage breakdown and humidity tests should be selected as most suitable for the comparison of various systems.

1. INTRODUCTION

Increasing density requirements require that the thick film hybrid manufacturers print high resolution patterns and also consider the application of multilayer hybrids. The introduction of compact interconnection technologies such as TAB and chip carrier will no doubt accelerate this process.[1]

Paste manufacturers are doing a lot of study in order to develop inks suited for fine line printing. The properties of dielectric pastes, necessary for multilayer applications, have not been studied that extensively.[2] A programme was started to compare various dielectrics in combination with various conductors. From the test programme two tests were found to be most significant for the dielectric's characterisation. These tests, in combination with an SEM-study of surface and bulk porosity, allowed a quick and reliable selection of an appropriate dielectric paste to be made.

2. EXPERIMENTAL

In a first stage, three conductors currently used by hybrid manufacturers were chosen for the tests, namely:

Du Pont 9061: a Ag/Pd fritted system, firing at 850°C [3]

Du Pont 9572: a Au/Pd fritted system, firing at 850°C

Du Pont 9910: an alloyed Au, mixed bonded system, firing at 925°C

These conductors are combined with three commercial dielectrics for cross-over (and multilayer) applications:

Du Pont 9429: a devitrifying system, firing at 850°C

Du Pont 9950: a devitrifying system, firing at 925°C

Engelhard 33.390: a "zero-flow" system, firing at 850°C [4]

Each conductor is combined with each dielectric; the top and bottom conductors are always the same. The aim of the investigation is to check if one of the dielectrics behaves better with all three conductors, and if cross-overs with Ag/Pd can be accepted.

The test pattern consists of two serpentine conductors, in a 90° angle, with a dielectric layer in between, in order to form a lot of cross-overs (256), (see Diagram)

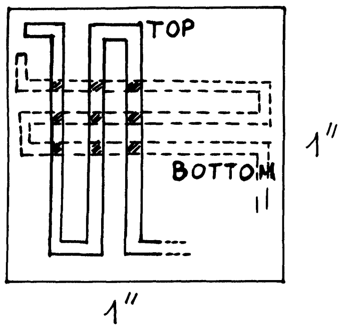


DIAGRAM OF TEST PATTERN

(conductor width: 500 microns
conductor spaces: 500 microns)

Substrates are 96% Al_2O_3 from Kyocera. Cross-overs are printed in two layers, each layer being separately dried and fired (total thickness: ± 40 microns). Cofiring of top conductors with the upper dielectric layer is not considered in this stage. Each layer is fired according to the manufacturer's specification.

For each of the nine combinations, 55 samples are prepared in order to perform the following tests:

5 samples: initial SEM-analysis and reference
10 samples: life test at 150°C
10 samples: temperature cycling test
10 samples: cold test and damp heat
10 samples: voltage breakdown test
10 samples: 85/85/60 test

In this stage of the programme all samples are unglazed and unencapsulated. In a further stage cross-overs are covered with glaze and some with glaze and Durez 9841 in order to get an idea of the degree of protection. Samples were prepared both in laboratory and production environments.

3. TEST RESULTS

3.1 Initial SEM and X-ray Analysis

By means of a JSM-35 scanning electron microprobe equipped with both energy- and wavelength-dispersive spectrometers all fired inks used have been thoroughly analyzed. The main results are:

DP 9572 consists mainly of Au and Pd, with some traces of Pt; as binder elements Pb, Si, B and Al are present (glass bonded).

DP 9061 consists mainly of Ag and Pd. Pb, Bi and Si are added for the adhesion (glass bonded). Traces of Mg and Cd are also detected.

DP 9910 consists mainly of Au, with a small addition of Pd (< 1%). Small amounts of Pb, Bi, Ca, Si (glass forming elements) and Cd (chemically bonding) are detected. This is a so-called "mixed-oxide bonding" system.

DP 9950 is a complex oxide of Al, Si, Ca (anorthite-type). Smaller amounts of Pb, K, Cd, Na and Mg are detected. These elements are also present as oxides.

Eng. 33.390 is a complex oxide of Pb, Al and Si. Smaller amounts of K, Ca, Cr, Cd and Mg – present as oxides – can be detected. Some chlorine has been found, which was verified by Engelhard: they claimed that the element Cl is introduced during the manufacturing of the glass powder. Action was taken to avoid this. High PbO contents in dielectrics may also cause troubles: when during firing, locally reducing conditions are present (as e.g. during the volatilization of hydrocarbons from the solvent) PbO may locally be reduced to metallic Pb-atoms, consequently decreasing the insulating properties of the dielectric.

DP 9429 consists mainly of $BaO.SiO_2$. Smaller amounts of Al, Ca, Zn, Mg and Ti are present as oxides. The same remark made for PbO is valid for ZnO; this oxide is easily reduced to metallic Zn.

Also by means of SEM, the surface of the three dielectrics has been characterized. Figure 1 shows the surface of DP 9950: almost no porosities are visible. Devitrifying of the glass partially occurs resulting in a crystalline phase (rectangular particles) homogeneously distributed.

At the surface of Eng. 33.390, only a few porosities are visible. The structure is very complex and the different phases can hardly be separated.

Figure 2 shows the surface of DP 9429: it is clear that this surface is very porous. It is a priori very probable that such a surface is not the best one for a dielectric. During processing the manufacturer's specifications were carefully observed, and we did not succeed in printing and firing a dense surface.

A third important feature readily to be observed from SEM-observations is the flow behaviour of the different pastes.

Figure 3 shows the varying width of top conductor DP 9910 over dielectric DP 9950. Under the dielectric layer marks are still visible, due to the level of the bottom conductor: after firing, the surface of the dielectric layer is not totally flat, the differences in level due to the bottom conductor still being present.

When the top conductor is screened, it flows out more readily in the "valleys" than on top. This effect enhances the risk of breakdown and reduces the critical migration distance between conductors. Figure 4 shows that this effect is related to the dielectric:

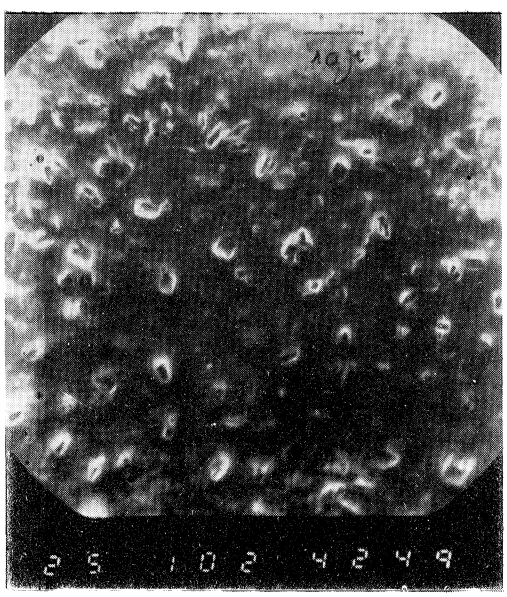


FIGURE 1 Surface aspect of DP 9950, Secondary electron image (25 kV).

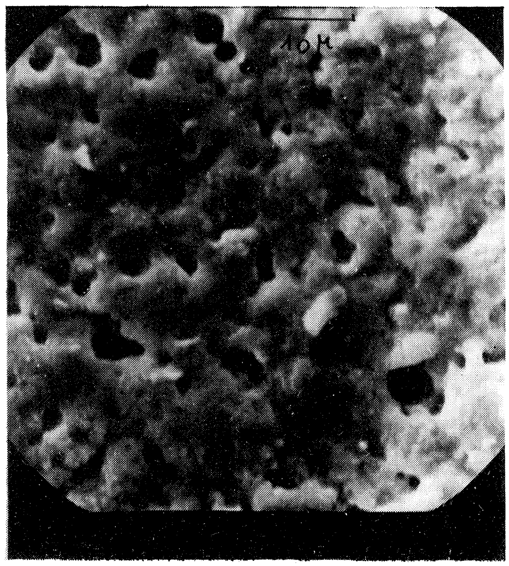


FIGURE 2 Surface aspect of DP 9429, Secondary electron image (25 kV).

Engelhard 33.390 forms a nearly flat dielectric layer. The bottom conductor is not visible anymore, and the variations in line width of the top conductor are negligible. DP 9429 behaves in a similar way as DP 9950, but to a less extent. Table I lists the minimum distances observed between two top conductors (nominally 500 microns):

Du Pont modified the 9950 dielectric at our request in order to improve its flow behaviour.

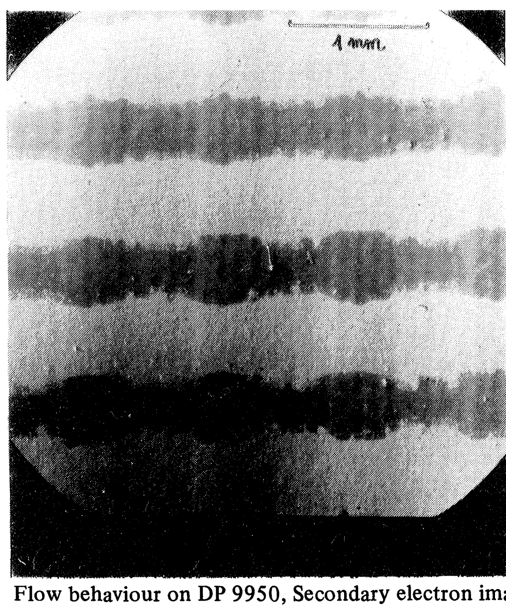


FIGURE 3 Flow behaviour on DP 9950, Secondary electron image (25 kV).

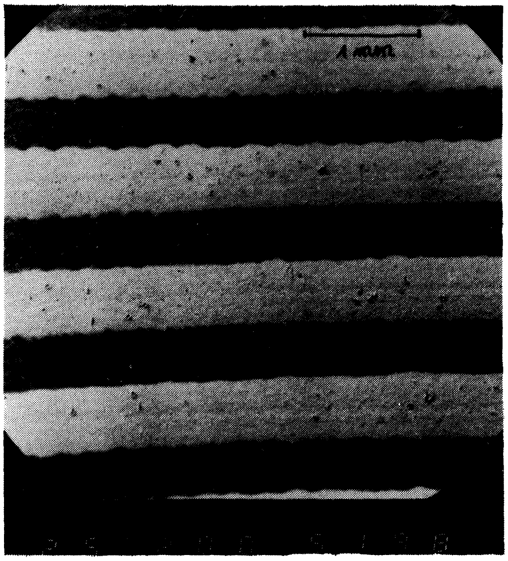


FIGURE 4 Flow behaviour on Eng. 33.390, Secondary electron image (25 kV).

TABLE I
Minimum distances observed between two top conductors (in microns)

	9572	9061	9910
9429	340	350	300
9950	300	300	175
33.390	360	420	370

A final observation readily made by means of SEM is the degree of bulk porosity. Samples are broken and the porosity of the dielectric is observed. Engelhard 33.390 turns out to be quite more porous than the two Du Pont materials. Figure 5 gives an idea of 33.390's porosity. This observation is far more rapid than from a full metallographic polishing process, and gives a valid image of the porosity throughout the fired dielectric.

3.2 *Life Test at 15°C*

Initial values of C are measured at 1 MHz, the insulation resistance Ri at 500 V (direct current). These values are compared with the results obtained after 300, 1000 and 2000 hours of ageing at 150°C. It is found that for a particular combination conductor/dielectric, C-values did not vary significantly during this test; the mean values are listed in Table II.

Taking into account our test configuration, these values correspond with some 4 pF/mm^2 and K-values of 15 - 19.

The proper series resistance of the conductors tracks largely attributed to the tgS-values, consequently we feel these values not to be realistic as dielectric losses.

The Ri-values for all combinations apparently decreased during the test, but to a different degree; the mean values decreased by the following factor (Table III):

The absolute values are always highest for 33.390.

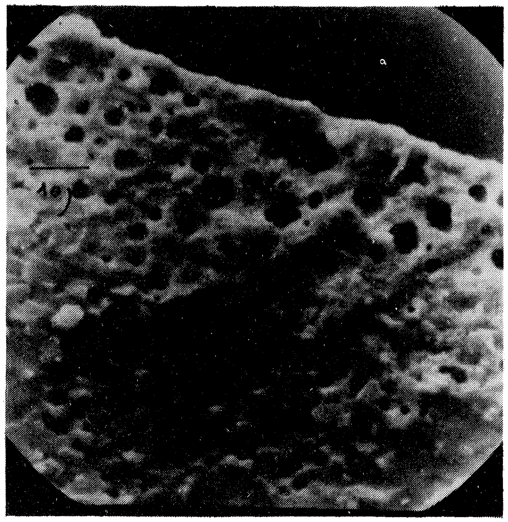


FIGURE 5 Bulk porosity of Engelhard 33.390, Secondary electron image (25 kV).

TABLE II
Average C-values of the 9 combinations (in pF)

	9572	9061	9910
9429	280	260	245
9950	280	250	220
33.390	260	240	215

TABLE III
Decrease factor of Ri during life test

	9572	9061	9910
9429	3, 7	2, 6	10
9950	3, 6	4, 1	2, 9
33.390	2, 7	3, 2	4, 2

3.3 Temperature Cycling Test

Five cycles –40°C/+85°C are applied on the specimens. As the changes after this test are minimal, additional cycles under more severe conditions (–55°C/+125°C) are done. Values of C and Ri are measured initially, and after 5, 30 and 100 cycles. The C-values correspond with 3.2, while for the Ri-values there is no definite tendency of decrease nor increase, except for DP 9429. One sample 9429/9910 was short after 5 cycles, and one 9429/9061 after 30 cycles.

3.4 Cold Test/Damp Heat

Values of C and Ri are measured initially, after 16 and 72 hours at –55°C, and after an additional "ageing" of 500 hours at 40°C/93 % R.H. Again the C-values do not vary significantly during the test. There is a clear tendency of Ri-decrease, which is mostly pronounced for DP 9429. Two samples 9429/9061 failed, three others had very low residual Ri values. Eng. 33.390 and DP 9950 decrease in a comparable way, but the absolute values for 33.390 are mostly higher.

3.5 Voltage Breakdown Test

An AC-voltage is applied to the samples and increased until breakdown. The mean values at breakdown are listed in Table IV.

TABLE IV
Mean voltage values at breakdown

	9572	9061	9910
9429	460	410	460
9950	1450	1300	1500
33.390	630	950	790

3.6 85/85/60 Test

Values of C and Ri are measured initially and after 500 and 1000 hours at 85°C/85 % R.H. and an applied 60 V (direct current). No meaningful variations of the C-values are observed. The insulation resistance decreases for all the samples, but to a different degree (after 500 hours):-

for DP 9950 the mean values decreased by a factor 4

for Eng. 33.390 the mean values decreased by a factor 8

for DP 9429 15 breakdowns occurred (on 29 samples)

The initial Ri-values are a factor 2 higher for 33.390 versus 9950, so the values after 500 hours correspond DP 9950 led to three breakdowns, 33.390 to one: these are all combinations with DP 9061. For DP 9429, all samples with 9061 failed, 40% with 9572 and 11% with 9910.

4. TEST RESULTS OF OTHER COMBINATIONS

From the test results discussed in Section (3), it is clear that the voltage breakdown and 85/85/60 tests are most meaningful as a way of comparison between different conductor/dielectric combinations. These tests are consequently selected for testing a lot of combinations which are suggested by thick film suppliers and/or based on experience.

The combinations tested are listed below:-

1) DP 9061/DP 9950 (repetition from previous tests)
2) DP 9061/DP 9429 (repetition from previous tests)
3) DP 9061/Eng. 33.390 (repetition from previous tests)
4) DP 9572/DP 9950 (repetition from previous tests)
5) DP 9572/DP 9429 (repetition from previous tests)
6) DP 9572/Eng. 33.390 (repetition from previous tests)

7) DP 9910/DP 9950 (repetition from previous tests)
8) DP 9910/DP 9429 (repetition from previous tests)
9) DP 9910/Eng. 33.390 (repetition from previous tests)
10) DP 9308/DP 9950
11) DP 9308/DP 9429
12) DP 9308/Eng. 33.390
13) DP 9061/DP 4032
14) DP 9572/DP 4032
15) DP 9910/DP 19120-123 (modification of DP 9950)
16) DP 9308/DP 4032
17) DP 9596/Eng. 33.390
18) DP 9596/DP 4032
19) DP 4019/DP 9950
20) DP 4019/DP 19120-123 (modification of DP 9950)
21) DP 4119/DP 9950
22) DP 4119/DP 19120-123 (modification of DP 9950)

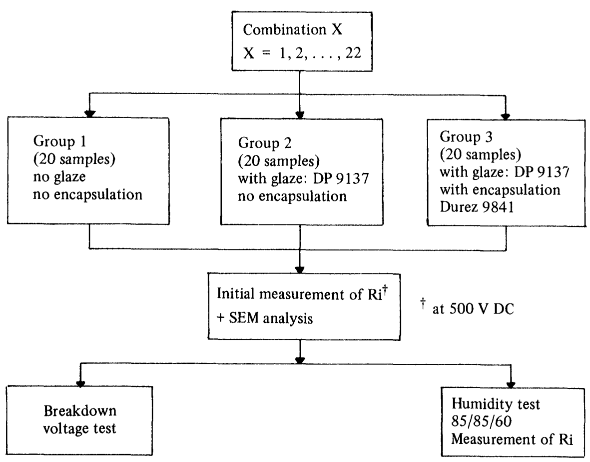
Combinations 1 to 9 are repeated in order to check the results of Section 2 on a new sample batch. Another Ag/Pd paste, DP 9308, similar to DP 9061 is combined with a number of dielectrics.

From the results of Section 2, it appears that DP 9429 is not acceptable as an 850°C-peak firing dielectric, and that the flow of a conductor on top of DP 9950 (a 925°C firing paste) is not optimum. Du Pont suggested trying another 850°C dielectric, namely DP 4032, and a modification of 9950, namely DP 19120-123. These materials are used in a number of combinations. DP 9596 is a Au/Pt conductor fired at 850°C and is sometimes used instead of gold for solderability reasons.

DP 4019 is a pure Au conductor, chemically bonded, with a low fired thickness (7-9 microns). DP 4119 is a Ag containing Au paste with reduced thickness (7-9 microns) and suitable for Al wire bonding.

Both materials are fired at 925°C peak temperature, and are both potentially interesting for multilayer applications.

In this section the efficiency of a protective layer is also checked. The test sequence is represented below:-



The principal results are summarized in a number of graphs.

4.1 Breakdown Voltage

Figures 6 and 7 show the results for the 22 combinations. These drawings are for the different combinations which represent separate points on the abscissa axis. In order to make a comparison easier, discrete results are interconnected.

The group 1 samples have the lowest breakdown voltage. Low results are obtained with DP 9596 conductor and DP 9429 dielectric.

A glaze protection on top increases the breakdown value generally with a few hundreds of volts, except for combinations with DP 9596 and combination 16. This may indicate a chemical reaction between conductor and dielectric which is independent of the protective layer.

There is a fairly good correspondence with Section 2; only the results for DP 9950 were significantly higher then.

4.2 Humidity Test

Figures 8 and 9 show the results of these tests. For group 1 samples, the insulation resistance (measured at 500 volts DC) is minimum 10^5 megohms, except for DP 9308/DP 9950. The insulation resistance is apparently higher for group 2 samples, but the Durez encapsulation has no further beneficial influence. The number of failures is:-

+ group 1: 14 (on ca. 220 samples)
+ group 2: 6 (on ca. 220 samples)
+ group 3: 15 (on ca. 220 samples)

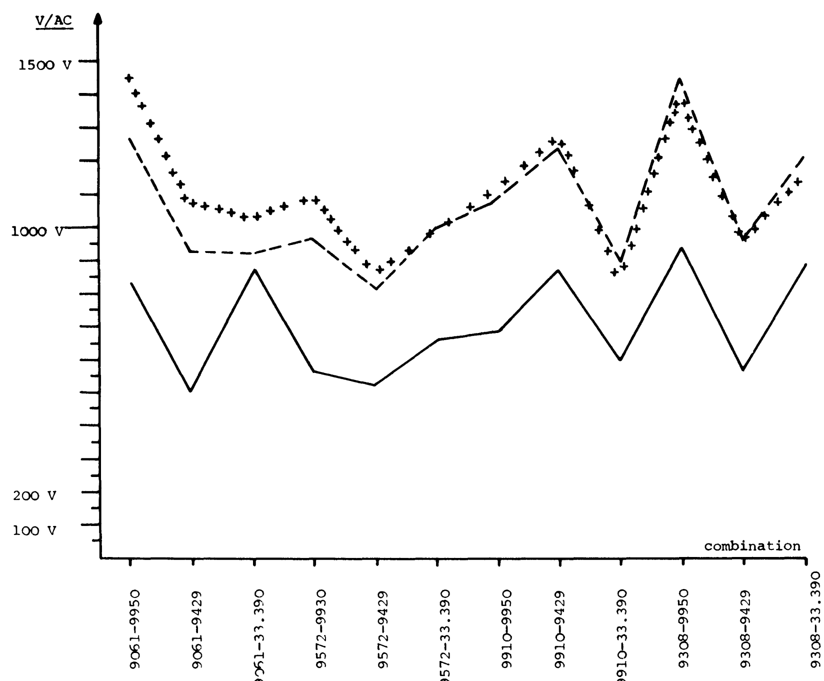


FIGURE 6 Breakdown voltage of various materials, ——— no glaze, no encapsulation, – – – – – – glaze DP 9137, no encapsulation, ++++++ glaze DP 9137, encapsulation Durez 9841.

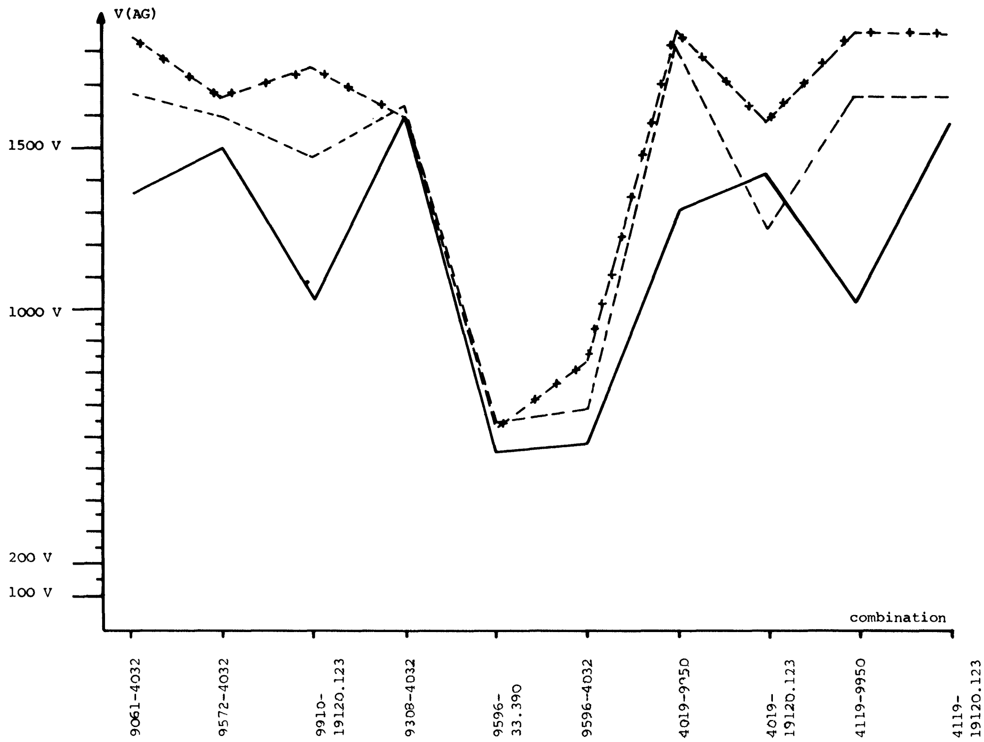


FIGURE 7 Breakdown voltage of various materials, ———— no glaze, no encapsulation, – – – – – – – glaze DP 9137, no encapsulation, ++++++ glaze DP 9137, encapsulation Durez 9841.

Failures per conductor:-

DP 9061:	8	(on ca. 120 samples)
DP 9308:	10	(on ca. 100 samples)
DP 9596:	12	(on ca. 60 samples)
DP 9572:	2	(on ca. 120 samples)
DP 9910:	3	(on ca. 100 samples)
DP 4019:	0	(on ca. 60 samples)
DP 4119:	0	(on ca. 60 samples)

The failure rate is clearly higher for Ag/Pd conductors DP 9061, DP 9308 (migration) and for DP 9596 (probably due to a chemical reaction between dielectric and conductor).

The Engelhard dielectric is apparently better in most combinations than the Du Pont dielectrics. Gold conductors 4019 and 4119 show no failures. DP 4032 is somewhat better (e.g. with DP 9061 and DP 9308) than the other Du Pont dielectrics.

4.3 SEM-Observations

4.3.1 DP 4032 is a complex oxide of Al, Si, Pb and Ca, in other proportions however than DP 9950. Oxides of Mg and Co are present in small quantities. Impurities such as Na and K are detected, but this could be due to processing contamination.

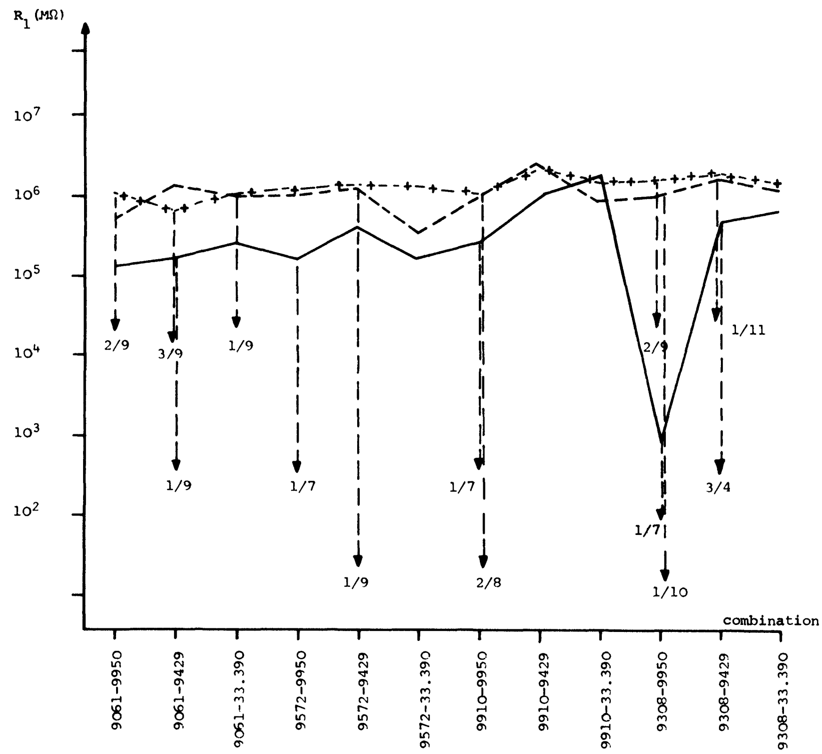


FIGURE 8 Results of humidity tests on various materials, ———— no glaze, no encapsulation, – – – – – – glaze DP 9137, no encapsulation, – – – – – – glaze DP 9137, no encapsulation, ++++++ glaze DP 9137, encapsulation Durez 9841.

Printability on top of this dielectric is rather poor as illustrated in Figures 10 and 11. The relatively good behaviour of this dielectric in humidity tests can be explained by the very low bulk porosity. (see Figure 12)

4.3.2 DP 19120-123 (DP 9950 Modification) The proportion of the main oxides (compared to DP 9950) appears to be somewhat different for this paste, although heterogeneity may influence this statement.

ZrO_2 is detected in the modified version (not in DP 9950). Printability on top of the modified paste is clearly better, as illustrated in Figure 13. The bulk porosity is however very high (Figure 14) which will cause problems in combinations with migration prone conductors.

5. DISCUSSION

The lack of availability of acceleration factors for these types of tests on hybrids prevents us at present from giving an estimated lifetime of the various cross-over and multilayer circuits.

Combinations with Ag/Pd conductors are only acceptable with Eng. 33.390, although the reliability level is not as good as for Au conductors; Au/Pt DP 9596 should not be

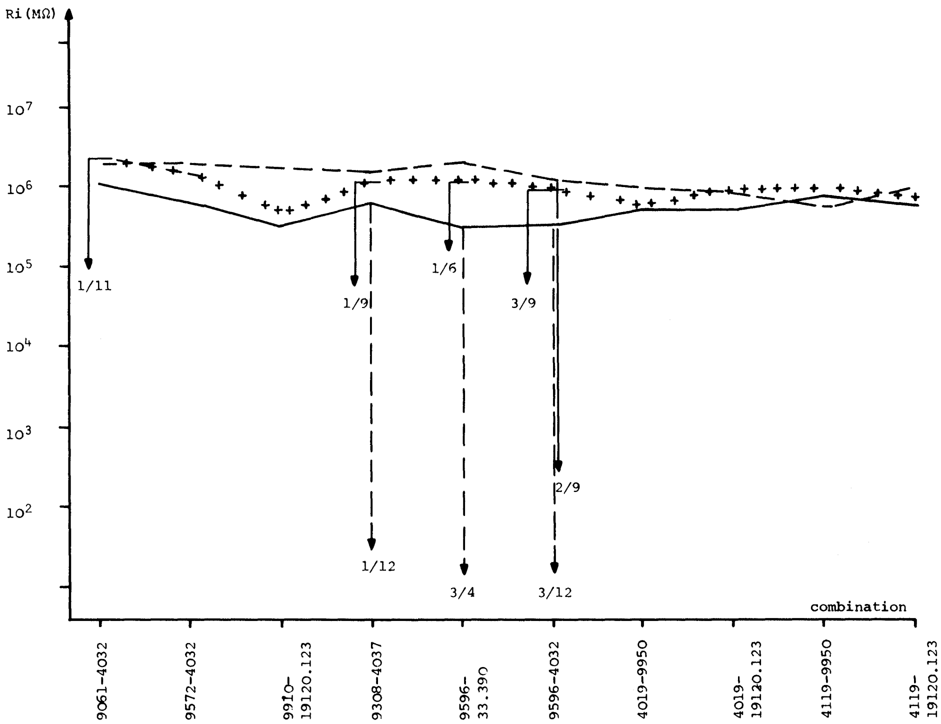


FIGURE 9 Results of humidity tests on various materials, ——— no glaze, no encapsulation, ------ glaze DP 9137, no encapsulation, ++++++ glaze DP 9137, encapsulation Durez 9841.

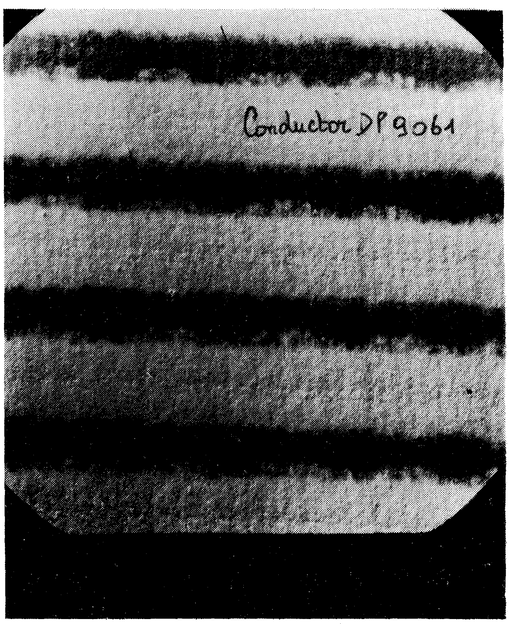


FIGURE 10 Poor printability of conductor DP 9061 on top of dielectric DP 4032 Magn: x20, Secondary electron image (25 kV).

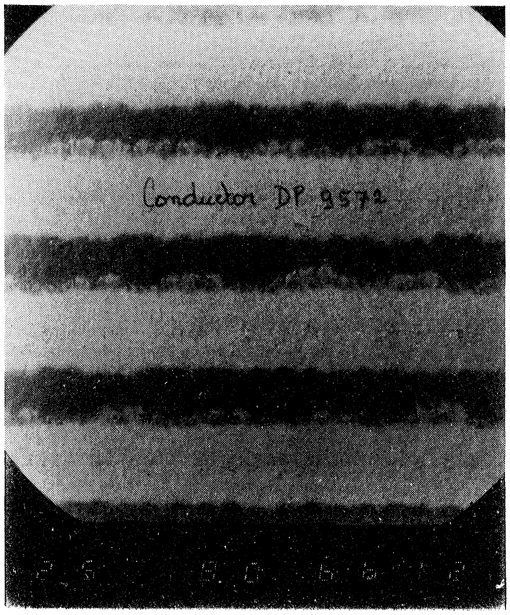


FIGURE 11 Poor printability of conductor DP 9572 on top of DP 4032 Magn: x18, Secondary electron image (25 kV).

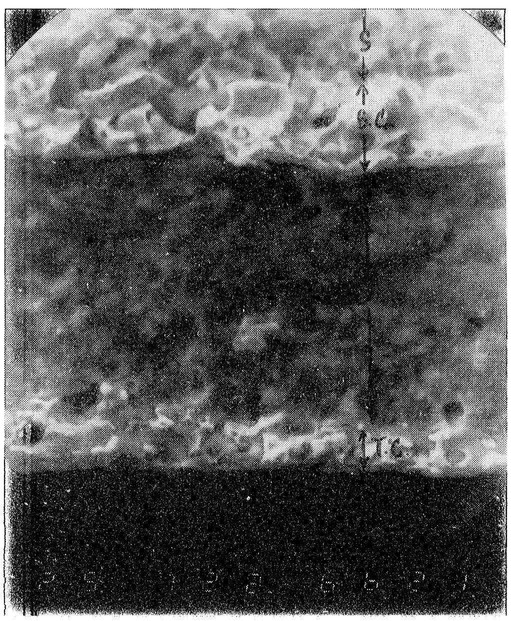


FIGURE 12 Cross-section showing low porosity of dielectric DP 4032.

T.G. = top conductor DP 9061
D. = dielectric DP 4032
B.G. = bottom conductor DP 9061
S. = substrate

Magn: x1200, Secondary electron image (25 kV).

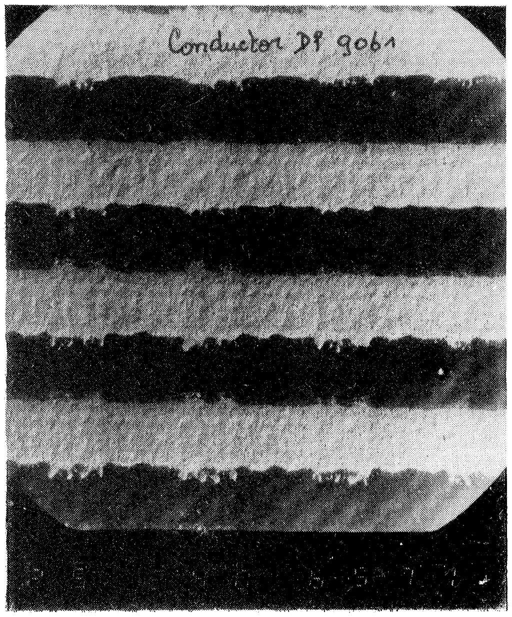


FIGURE 13 Printability on top of 19120-123; conductor is DP 9061, Magn: x24, Secondary electron image (25 kV).

FIGURE 14 Cross-section showing high porosity of dielectric DP 19120-123. Magn: x1200, Secondary electron image (25 kV).

used in cross-overs. Au conductors DP 4019 and DP 4119 are quite reliable even with porous dielectrics (DP 1920–123).

Dielectric DP 9429 has a very porous surface as observed by means of SEM. The "efficient thickness" of the fired dielectric is consequently reduced which explains the low breakdown voltage, and the poor behaviour in environmental tests. The bulk porosity of Eng. 33.390 explains the higher degradation rate during 85/85/60 test, and its lower breakdown voltage. The paste has however better flow characteristics than DP 9950, which is important in multilayer applications with fairly close conductor tracks.

Dielectric DP 4032 is an improvement versus DP 9429 but poor printability on top of it is still a weak factor.

The improvement version of DP 9950 is actually better in terms of printability but will cause migration problems due to its higher bulk porosity.

6. CONCLUSIONS

SEM-observation and analysis provide a quick and reliable method of predicting the cross-over and multilayer characteristics of a dielectric paste. Surface and bulk porosity, flow behaviour and chemical composition, determined by SEM are closely related to the results of electrical and environmental tests. From the latter, voltage breakdown and humidity tests should be selected as most suitable for the comparison of various systems.

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