EFFECTS OF PARTICLE SIZE DISTRIBUTION IN THICK FILM CONDUCTORS

Robert W. Vest
Purdue University
West Lafayette, Indiana 47907

INTRODUCTION

The packing of particles for maximum density is a problem of great importance in ceramic processing and powder metallurgy, but it is even more critical in thick film conductors because of the very low compacting pressures exerted during screen printing. The fired film density, and hence the electrical resistivity, is intimately related to the density of the metal compact which exists after the organic constituents of the ink have been removed in the early stages of firing. This green density is even more important if the firing cannot be carried out at a sufficiently high temperature due to limitations imposed by the substrate. The coordination number (CN) and the fractional porosity (P) for the packing of spherical particles is shown on page 2 for various geometries. The case of random packing is of most interest, and previous workers have distinguished two types - dense and loose random packing. The coordination numbers shown on page 2 for these two cases were experimentally obtained as were the porosity numbers. The porosity of 0.363 also given for dense random packing, was obtained by computer simulation.

THEORETICAL MODELS

A distribution of particle sizes can be used to decrease the porosity associated with packing of monosized spheres. The two primary approaches that have been taken to modeling this problem are shown on page 3. With approach A, a single sphere of the largest possible size is inserted to fill the interstices in the packed bed. Approach B inserts many very small particles to fill the porosity. The methods of modeling with Approach A are given on page 4. Since the experimental coordination numbers obtained for random packing are close to that of body center cubic packing, one can assume BCC and fill all of the tetrahedral sites with small spheres. Since this is a regular geometric packing, the ratio of sizes of the spheres can be exactly calculated as 0.291. The volume fraction of smaller spheres to exactly fill all the tetrahedral sites is 0.129, giving a porosity for the two sized system of 0.219. However, the packing is not really body centered cubic, and the best approach to determining the size and quantity of spheres to add is by computer modeling. The model developed by approach B is described on page 5. If it is assumed that the second size sphere is very small compared to the first, then all of them can go into the porosity of the larger spheres. Since the porosity of any packed bed depends only on the coordination number, it can be assumed that the fractional porosity in each size fraction is the same. With these two assumptions, the volume fraction of the small size can be calculated in terms of the porosity for
packing of the larger size. The final porosity turns out to be simply the square of the porosity of one size. This model can easily be extended to many different sizes of particles as shown on page 6.

The results from applying approach A and approach B to two sizes of spheres are summarized on page 7 for different packing geometries of the large size. The calculations are exact for the simple cubic and body centered cubic packing. The volume fractions and porosities given for the dense random and loose random packings were calculated using the equations on page 5 and the appropriate porosity from page 2 for approach B, and by computer modeling for approach A. For approach B, the ratio between the diameter of the smaller and the larger spheres should be very small, and for the loose random packing, this ratio should be less than 0.006. The origin of this number is described on page 8 in terms of a hypothetical experiment; to start with a layer of small spheres on top of a layer of large spheres, and then mix the two sizes and calculate the change in volume. A parameter y, which is a function of ratio of particle sizes, is introduced, and an experimental value of y is utilized to calculate the porosity in terms of the ratios of solid volumes and ratios of solid diameters. This equation is plotted on page 9 as the porosity as a function of volume fraction with size ratio as a parameter. At the optimum volume fraction, the porosity is 0.16 as predicted for loose random packing if the ratio d_2/d_1 is zero. If this ratio is 0.006, the porosity becomes 0.17. Previous researchers have stated that the approach B model can be utilized as long as the ratio of sizes is less than 0.2, but the plot on page 9 shows that the correction at 0.2 is very large. A difficulty with either approach A or B is the uniformity of mixing of the two sizes, and this problem has been addressed by introducing a mixedness parameter (M) as described on page 10. Values of M can only be obtained experimental.

There are some special problems in applying the theoretical models to thick film conductors as listed on page 12. No one has studied the mixedness parameter for roll mill blending of thick film inks, so no values are available for correction factors. For all thick film conductors, at least one additional phase is added in order to develop adequate adhesion to the substrate. Even though the glass frit or base metal oxides are present in small concentrations relative to the metal, they still can influence the packing of the metal particles. The thickness of the films is also a special problem because container effects have been observed in studies of random packing of spheres.

**EXPERIMENTAL CONDUCTORS**

A platinum thick film conductor having the requirements listed on page 13 was needed for a project in the Turner Laboratory at Purdue University. It was decided to try approach B to achieve high density using three different size platinum particles. In order to achieve the desired ratio between diameters of successive size ranges, the smallest size was formed in situ by decomposing a platinum resinate. The variation of grain size with firing temperature of the resin e is shown on page 14. The size 0.02 μm was assumed for particles from t is source because that was the grain size corresponding to the temperature at which all of the organics had been re-
moved. The results obtained with eight different inks are given on page 15. The uniformity and porosity of the films were the primary criteria used for judging quality. The optimum volume fractions of three sizes as predicted by the model for approach B is 64-26-10, as given on page 6. This ink did give lower porosity than any of the one or two size inks studied, but was not as good as the last two inks on page 15. These inks had compositions arrived at empirically. The difference in microstructure between the inks at the top and bottom of page 15 are shown on page 16, and it is obvious that selection of particle sizes of the conductor can make a very significant difference in film microstructure.

Another experimental program had the goal to develop silver conductors with the requirements given on page 17. This was for a consumer application, and cost was a very significant factor. The primary criterion used for evaluating various inks was the conductance per gram of silver, or the specific conductance as defined on page 18. If one takes the ratio between the specific conductance of two films, the result is independent of the film geometry. The silver inks were formulated as described on page 19, and the results with 6 different mixture of particle sizes are given on page 20. Ink 6, which contained only silver particles 17 µm diameter, was not an electrical conductor because the very large silver particles did not sinter during the firing at 625°C for 10 minutes. The ratio of 70-28-2 for the fractions of three different sizes in inks 1, 2 and 3 is close to that predicted by the theoretical model of approach B, but was arrived at empirically. It can be seen from page 20 that ink No. 1 with three sizes of silver particles had a higher specific conductivity of any of the films with only single size particles, but the other two mixtures did not have as high a specific conductivity as two of the monosized inks. The ratio between successive sizes for the three mixed size inks is shown on page 21 along with the specific conductivity ratio. These results reflect the influence of the absolute size of the largest silver particles and its influence on sintering, as well as the effect of the ratio of sizes, particularly between the largest and next largest (d2/d1). The size ratios for ink No. 1 are close to those calculated for dense random packing by approach A (see page 7).

SUMMARY

The conclusions that can be drawn from the studies of particle size distribution in thick film conductors are summarized on page 22. The distribution of particle sizes does have an effect on fired film density but the effect is not always positive. A proper distribution of sizes is necessary, and while the theoretical models can serve as guides to selecting this proper distribution, improved densities can be achieved by empirical variations from the predictions of the models.
### Page 2. Packing of Spheres

<table>
<thead>
<tr>
<th>GEOMETRY</th>
<th>CN</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>Closest Packed</td>
<td>12</td>
<td>0.26</td>
</tr>
<tr>
<td>Body Centered Cubic</td>
<td>8</td>
<td>0.32</td>
</tr>
<tr>
<td>Simple Cubic</td>
<td>6</td>
<td>0.48</td>
</tr>
<tr>
<td>Dense Random</td>
<td>8.5$^a$</td>
<td>0.363$^c$</td>
</tr>
<tr>
<td>Loose Random</td>
<td>7.1$^a$</td>
<td>0.40$^b$</td>
</tr>
</tbody>
</table>

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### Page 3. Two Models for Packing Two Sizes of Spheres

![Diagram showing two models for packing two sizes of spheres.](image-url)

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Page 4. Approach A

1. Assume BCC since CN = 7.1 - 8.5

N spheres (d₁) in BCC packing

6N tetrahedral sites
3N octahedral sites

fill the larger tetrahedral sites with spheres (d₂)

\[ \frac{d₂}{d₁} = 0.291 \]

\[ \sqrt{v₂} = 0.129 \]

Porosity = 0.219

2. Computer Modeling

Best Approach
Page 5. Approach B

$V_1, V_2$ - solid volume of each size

$P_1, P_2$ - pore volume associated with each size

Assume size 2 goes into the porosity of size 1 ($d_2/d_1$ very small)

$$V_2 + P_2 = P_1 \quad (1)$$

Assume size 1 and size 2 have the same packing. Then the pore fraction will be the same.

$$P = \frac{P_1}{V_1 + P_1} = \frac{P_2}{V_2 + P_2} \quad (2)$$

Combining Eqs. 1 and 2 gives

$$\frac{V_2}{V_1} = P \quad (3)$$

$$\frac{V_2}{V_1 + V_2} = \frac{P}{1 + P} \quad (4)$$

Porosity $= 1 - \frac{V_1 + V_2}{V_1 + P_1} = P^2 \quad (5)$
Page 6. Approach B (Cont’d)

Sizes 1, 2, 3, ..., i, ..., n

Assume \( d_{i+1}/d_i < 0.01 \)

\[ V_{i+1} + P_{i+1} = P_i \]

Assume all sizes have the same packing

\[ P = \frac{d_i}{V_i + P_i} \]

Then

\[ V_{i+1}/V_i = P \]

And in general

\[ \frac{\nu_i}{\nu_i} = \frac{p^{i-1}}{p^0} \]

Example

3 sizes, \( P = 0.4 \)

\( \nu_1 = 0.64 \)

\( \nu_2 = 0.26 \)

\( \nu_3 = 0.10 \)

Page 7. Two Sizes of Spheres

<table>
<thead>
<tr>
<th>Packing of Size 1</th>
<th>( \nu_2 )</th>
<th>( d_2/d_1 )</th>
<th>Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>A</td>
</tr>
<tr>
<td>Simple Cubic</td>
<td>0.28</td>
<td>0.32</td>
<td>0.73</td>
</tr>
<tr>
<td>Body Centered Cubic</td>
<td>0.13</td>
<td>0.24</td>
<td>0.29</td>
</tr>
<tr>
<td>Dense Random</td>
<td>0.17*</td>
<td>0.27</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>made</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.26*</td>
</tr>
<tr>
<td>Loose Random</td>
<td>-</td>
<td>0.29</td>
<td>&lt;0.006</td>
</tr>
</tbody>
</table>

Page 3. Approach B: Layered Bed

\[ \text{Volume} = V_2 + P_2 \]
\[ \text{Volume} = V_1 + P_1 \]

\[ p = \frac{P_1}{P_1 + V_1} = \frac{P_2}{P_2 + V_2} \]

\[ \text{IX THE TWO SIZES} \]
\[ \Delta V_{\text{max}} = V_2 + P_2 = \frac{V_2}{1-p} \]
\[ \Delta V - y \Delta V_{\text{max}} \]
\[ y = 1 \text{ for } d_2/d_1 = 0 \]
\[ y = 0 \text{ for } d_2/d_1 = 1 \]

experimentally * \[ y = 1 - 2.62 \left( \frac{d_2}{d_1} \right) + 1.62 \left( \frac{d_2}{d_1} \right)^2 \]

\[ \frac{V_1 + V_2}{V_1 + P_1 + V_2 + P_2 - \Delta V} \]
\[ \text{Porosity} \]
\[ \frac{\{1 + V_2/V_1\} - y V_2/V_1}{\text{Porosity} \cdot \{1 + V_2/V_1\} - y V_2/V_1} \]

*C.C. Furnas, Ind. Eng. Chem., 23, 1052 (1931)*
Page 9. Effect of Size Ratio on Porosity With Approach B

![Graph showing the effect of size ratio on porosity.](image)

The graph illustrates the relationship between the size ratio (d2/d1) and the porosity (Vp/Vl) for different values of d2/d1. The x-axis represents V2/Vl, and the y-axis represents the porosity (Vp/Vl). The lines indicate the porosity values for different size ratio values.
Page 10. Uniformity of Mixing

A problem for Approaches A and B

Introduce a degree of mixedness parameter (\(M\))

\[
M = 1 - \frac{\sigma}{\sqrt{\nu_2(1-V_2)^{1/2}}}
\]

\(\sigma\) = std. deviation of compositional variations

A proposed relationship is

\[
B = B_u + M^2(B_m - B_u)
\]

where \(B\), \(B_u\) and \(B_m\) are bulk densities of real mixtures, a fully unmixed system, and an ideally mixed system, respectively.

Later work has shown that \(M\) and \(B\) (or final porosity) are not uniquely related, and a statistical approach must be taken.


Page 11.

Theoretical studies predict and experimental studies confirm that the maximum corrections due to \(M\) occur near the optimum values of \(\nu_2\) predicted by either Approach A or Approach B.

Typical powder mixing techniques give \(M\) values of 0.77 to 0.96.

\(M\) values for roll mill blending of thick film inks?


Page 12. Special Problems With TF Conductors

Mixedness

Presence of Glass Frit

Availability of Sized Powders

Alloying Reactions

Film Thickness

Page 13. Platinum TF Conductors

Requirements

1. No metal other than platinum

2. Single print

3. Highest possible density

4. Highest possible uniformity

5. Fire at 850°C (0.55 T_m) on alumina
Page 14. Variation of Grain Sizes With Firing Temperature of Platinum Resinate

Firing Time - 10 minutes
Page 15. Platinum Powders

$d_1 - 30 \ \mu m$
$d_2 - 1 \ \mu m$
$d_3 - 0.02 \ \mu m$ (from resinate)

Experimental Platinum Conductors Fired at $850^\circ C$.

<table>
<thead>
<tr>
<th>$d_1$</th>
<th>$d_2$</th>
<th>$d_3$</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td></td>
<td></td>
<td>very porous, large open areas</td>
</tr>
<tr>
<td>100</td>
<td>50</td>
<td></td>
<td>very porous, uniform</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td></td>
<td>large open areas</td>
</tr>
<tr>
<td>50</td>
<td>20</td>
<td></td>
<td>closed pores</td>
</tr>
<tr>
<td>90</td>
<td>10</td>
<td></td>
<td>low porosity</td>
</tr>
<tr>
<td>64</td>
<td>26</td>
<td>10</td>
<td>lower porosity</td>
</tr>
<tr>
<td>87</td>
<td>9</td>
<td>4</td>
<td>very low porosity</td>
</tr>
<tr>
<td>88</td>
<td>10</td>
<td>2</td>
<td>lowest porosity</td>
</tr>
</tbody>
</table>
Page 16. Experimental Platinum Conductors in Transmitted Light (190X)

100% \( d_2 \)

88% \( d_1 \) - 10% \( d_2 \) - 2% \( d_3 \)
Page 17. Silver TF Conductors

Requirements

1. Lowest possible cost (highest possible specific conductance)

2. Single print

3. Very uniform films

4. Fire at 629°C (0.73 T_m) on POS

Page 18. Specific Conductance Ratio (SCR)

specific conductance = SC = \frac{G}{W}

G = conductance of film
W = weight of film

\[ SC = \frac{1}{RW} - \frac{1}{PD^2} \]

p = film resistivity
d = film density
A = film length

\[ (SCR)_{i,j} = \frac{(SC)_i}{(SC)_j} - \frac{\rho_i d_i}{\rho_j d_j} \]

Independent of film geometry
Inorganic Constituents

1. 95 w/o silver of various particle sizes or mixtures of different particle sizes

2. 5 w/o glass of composition 72 w/o PbO - 14 w/o B$_2$O$_3$ - 14 w/o SiO$_2$ sieved to -170 mesh

Screening Agent

1. 3 w/o ethel cellulose (N-300)

2. 97 w/o α-terpineol

Page 20. Composition and Specific Conductance of Silver Films

<table>
<thead>
<tr>
<th>Ink No.</th>
<th>% of Ag Particle Sizes (μm)</th>
<th>SC (S/mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>.65</td>
<td>2</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>28</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>28</td>
</tr>
<tr>
<td>3</td>
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<td>4</td>
<td>100</td>
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<tr>
<td>5</td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Page 21. Particle Size Ratios and Specific Conductance Ratios of Silver Films

<table>
<thead>
<tr>
<th>Ink No.</th>
<th>Size Ratios</th>
<th>((SCR)_1), Ink no.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(d_2/d_1)</td>
<td>(d_3/d_2)</td>
</tr>
<tr>
<td>1</td>
<td>.29</td>
<td>.33</td>
</tr>
<tr>
<td>2</td>
<td>.12</td>
<td>.33</td>
</tr>
<tr>
<td>3</td>
<td>.43</td>
<td>.13</td>
</tr>
</tbody>
</table>

Page 22. Summary

1. The distribution of metal particle sizes and the absolute sizes affect fired film density.

2. The proper distribution of metal particle sizes gives a higher density film than single sized particles.

3. The theoretical models can serve as guides to selecting the proper distribution of metal particle sizes.

4. Experimental studies are still required.
DISCUSSION

WONG: I think probably in the real world you make a very fine particle and use coarse particles in your mix, and the very fine particles try to stick together and agglomerate by electrostatic forces, or align, so that is why you never have a mix completely as what you assume in the model.

VEST: That certainly is true. In the platinum case, the second size I said were 1 micron. Well, the 1-micron were the agglomerate size. This was a platinum black, and the ultimate particle size was a few hundred Angstroms. Just because of what you were mentioning: there was agglomeration, and the agglomerate sizes were just about 1 micron. We got this from SEM studies. Yes, that certainly is true.

WONG: In your model you are mixing two sizes, and this small particle size is supposed to fit in the hole. What if you just assumed that there is no mass transport -- no sintering mass transport occurring -- however, if you, from a sintering viewpoint, just use a fine particle size, just a single particle size, would that be better from a sintering viewpoint, from thermodynamics?

VEST: If you can get a high enough compaction to start with and you can go to the proper temperatures, a single-size, a small-enough-sized particle can give you very high densities of sintered mass, but if you have some constraints on your processing, then you can do better with a gradation of sizes. The presence of smaller spheres in the interstices of the bigger ones will enhance the sintering of the bigger ones, because as the smaller ones begin sintering they are also in contact with the big ones and they will attach themselves. So, as they begin to shrink, they give a compressive force to the bigger spheres and make them sinter more rapidly. So you get enhanced sintering of the larger size due to the presence of the smaller size.

WONG: Again you have to assume that the small sizes go into the interstitial sites of the bigger ones.

VEST: That is right. Again, if you are making a large body, using a single size, small size particle has many advantages, but for our conductors we don't want them to change dimensions very much during firing. We want to keep our good line definition, so it is nice to have these big ones there, big particles that are forming the matrix, and then this isn't going to change much. But then if we can fill up the holes in this with smaller ones, enhance the sintering of the bigger ones, then we get closer to what we want.

AMICK: Could you comment on why the 17-micron particles don't work better than the 7 in that silver-ink composition?

VEST: It is because they are too big. The 17 by itself did not sinter; the mix did, and we get a number.

AMICK: You have a bigger ratio difference with the 17 than you did with the 7?
VEST: That is right. You have a bigger ratio difference but you are still not getting as much sintering of the big ones, which constitute the bulk of the silver, with the 17s as you are with the 7s. In other words, these results, I think, are indicative of the fact that you still have very poor sintering of the large particles, so that you have a lot of constriction resistance. You have very small sintered necks between the big particles and so you are getting constriction resistance that is limiting the conductance. The presence of the small particles did exert a force, an influence, in getting sintering but still not as much as you get starting with a 7-micron largest size.

AMICK: Do you alter the ratio to binder for those two different materials? Is there binder in these systems?

VEST: Oh, yes. Well, there was when it was printed. There was a screening agent used for printing.

AMICK: Is there glass also?

VEST: Oh, yes. And it is the same in all of these.

AMICK: The same ratio?

VEST: Yes. The same ratio of metal to binder.

GALLAGHER: In the real world, in some of these soft metals like silver, how close are they to being spherical?

VEST: These particles are very spherical. They are prepared that way; the ones that I used. You can get spheres, you can get flake, you can get all kinds of things.

GALLAGHER: My second question involves flake. I think I have seen somewhere where spherical powders have been mixed with flake. What is the rationale behind that?

VEST: You have these flat plates lying here, and you have little ball bearing between them; you get good contact. That is the rationale I have heard used for the adding the mixture of flake and powder to simply a polymeric binder where you are not firing, really. You get higher pressure contacts when you have the little spheres contacting the flake, so you will get continuity. You will break through the stearate coating that had been on the silvers.

GALLAGHER: Would you care to comment on that stearate coating?

VEST: Well, it is there. It is not a good electrical conductor. Somehow you have to overcome this in order to get good conduction.

GALLAGHER: Do you do it thermally, or is it a trick of the trade? Any reason people don't talk about it?

VEST: I don't know. There are some people here that could probably comment on that but I am not one of them.
STEIN: I think it is a trick of the trade.

GALLAGHER: And here I thought only the plating people had problems and didn't want to talk about it.

LANDEL: Regarding the question that was asked a moment ago about the 17- and 7-micron particles. Does the smaller particle in fact give you a lower sintering temperature? Is it small enough to get particle size effects?

VEST: Well, of course.

LANDEL: The difference between 17 and 7. Does that lower the sintering temperature? If you just take that individual particle size and you work with 17 and you work with 7 --

VEST: I would end up with a larger ratio of sintered neck diameter to particle diameter for the 7 than for the 17 at the 6-25-10 minutes. That was the boundary condition on our process.

LANDEL: Then that is the answer there. The smaller particle size, in fact, is easier to sinter. It has a higher surface energy and therefore it is easier to sinter. Sinters at a lower temperature.

COMMENT: That is really quite a different model from the one that was proposed.

LANDEL: Well, yes. That is an added effect. It would have to be run in.

VEST: Certainly. You see, with the 17s by themselves, there was not sufficient sintering at these conditions to even form a continuous network. Whereas with a 7, there was. Just looking at those results for monosized powders you can tell we have a definite difference in sintering with these different sizes at that temperature.

LANDEL: Do you measure the packing density of the dry powders, and if so, can you use that in your evaluation?

VEST: I would love to. I don't know how. I have looked at the density of the packed powder before sintering. If you very carefully dry, so as to remove all the organics without getting any sintering -- and you can do this, if you are very careful, and then, of course, you have to be very careful in handling because the stuff would fall off the substrate -- but I don't know of a way of measuring the density of that powder compact. You know it has to be somewhat more dense than simple cubic. It is somewhere between there and body-sintered cubic.

LANDEL: For the spheres it would be, ideally, 0.63.

VEST: Yes, if it was closest packed.

LANDEL: Random packing.

VEST: OK, for random packing.
LANDEL: Then someone said that if you get the small particle sizes then the agglomeration drives that up again, or drives that down in terms of packing density, to something like 80.4. You have to trade off those factors.

VEST: Yes. Again we measure things such as dried-film density or dried-film thickness, but that is not something that you can really measure very accurately. You can measure the fired-film thickness quite well. The dried-film thickness doesn't have a smooth surface. You have particles there, so you can use a light section microscope and you try to sit on top of one, but there is a lot of uncertainty in the measurement. Certainly, within what we have measured, it comes down to this loose, random packing. But there is quite a bit of scatter.

STEIN: A further comment on Brian's (Gallagher) question, which really deserves a bit more of an answer. That is, when you try to sinter particles that are coated with stearates or other things, they are not going to sinter very well -- particularly in the instance of people in this room who are firing very quickly for very short times at temperatures in the order of 700°C. Some of the organics can remain at temperatures higher than that, or else need a longer time than a minute or two to be gotten rid of. As long as they are present they will interfere with sintering. In the case of mixed spherical and platelike or flakelike particles, you have some relatively clean particles, you have some relatively dirty particles and you have all kinds of surface things; therefore, you get a combination of decomposition products coming off, sintering occurring simultaneously, and never, never do you have a completely organic burned-out system if you are firing for 30 seconds or one minute or so at 700°C or 720°C, or some such short time at a relatively low temperature. This is particularly different from the thick-film hybrid microelectronics case where they are firing up at 850°C or more, and you have ample time to burn out. Infrared firing is an example that makes this problem very difficult and should you get sintering of the silver, before reaching full burnout conditions, you are going to blow blisters and bubbles.

GALLAGHER: Has one ever put a mass spectro on the end of the furnace to see some other decomposition products? Just a general question to anybody.

STEIN: There are all sorts of hydrocarbon fragments. It has not been done at the end of a furnace, but it has been done. You get CO, CO₂, free-radical type fragments in the methyl and ethyl groups, and all sorts of things coming off. It is a wild mixture. It depends very much on the access of air. How much air you have available.

GALLAGHER: Does that mean that with some of these inks we have to force air into the furnace rather than just have a free air flow?

STEIN: Absolutely.

VEST: The air flow is one of the principal variables in the processing.
SOMBERG: I would like to ask a question of Sid (Stein). You mentioned that some of the organics are still remaining with the spike firing. If I am going through a burnout phase, am I not getting burn out between 300°C and 550°C? I am referring to spike firing at 700°C, but I am still going through burnout between 400°C and 500°C. Why am I not getting rid of the organics at that point?

STEIN: Because the organics that are closest to the silver surface, in case of the silver, or to any metallic particle surface, are remarkably stable. At least you don't fully get rid of them. That monomolecular layer of materials stays there, well beyond the normal decomposition ranges that one expects.

COMMENT: It is even difficult to remove all the water from the surfaces on the silicon.

LANDEL: Plus, if it is stearic acid you are trying to remove, you are trying to decompose not with an organic but with a metal organic, so you are trying to decompose a salt.