

N84 21992 *D12*

PARTICLE SIZE EFFECTS ON VISCOSITY OF SILVER PASTES --- A MANUFACTURER'S VIEW

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I. INTRODUCTION

The electrical performance of single crystal silicon in photovoltaics with thick film silver forming the top metallization grid is well documented. Silver, the major component, however, is often taken for granted. There are several dozen types of silver powders commercially available for use in thick film silver paste (ink) systems. The basic properties of these powders are reasonably well documented. A study was made to characterize some of these powders in actual applications and correlate this information with the viscosity and rheological properties of pastes under shear.

II. EXPERIMENTAL

A. Materials: Seven commercially available silver powders, representing a cross section of particle sizes and shapes, were selected for investigation in experimental thick film conductor pastes. A glass used in commercial silver paste compositions was also prepared in three powder sizes for study in experimental glass pastes. Pastes were prepared by combining these silver and glass powders with an identical organic screening vehicle and homogenized on a standard three-roll mill. Organic vehicles with varying properties to adjust paste rheology were from the same family of compositions. Solids content was held constant at 80% for each of the silver and glass pastes.

Silver pastes were screen printed by standard methods, subjected to infrared drying at 125°C and fired in a belt furnace at 850°C. This temperature, higher than normally used in actual cell production, was selected to dramatize particle effects on sintered films.

B. Particle Size Analyses: Particle analyses to determine particle sizes, distribution of particles and volume populations were performed with a Coulter Counter, Model TA II. A 50µm aperture, capable of accurate particle measurement from 0.8 to 20µm, was selected as optimum for the cross section of sizes investigated. Tap density data were supplied by the manufacturers of the silver powders.

C. Scanning Electron Micrographs: Micrographs were prepared at 2000X with an AMR, Model No. 1000A Scanning Electron Microscope. For consolidating comparisons, magnifications were reduced, as shown in the figures.

D. Viscosity-Rheology Tests: Viscosity measurements were made with a Wells-Brookfield Micro Viscometer (cone-plate), Model HBT, with a 1.565°C cone. Test temperature was maintained at 25±0.2°C. Rheological properties were computed from viscosity data taken at shear rates from 1.92 to 19.20

reciprocal seconds with a Hewlett Packard Model 9825T Computer which plotted the curves with a H.P. Model 7225A Plotter.

### III. RESULTS AND DISCUSSION

Particle size, particle shape and volume populations have a strong influence on the rheology, and thus the screen printing characteristics of silver pastes. A change in surface area from a change in particle size, shape or population can cause problems in the way the paste prints and contacts the silicon surface. Incomplete line traces or pin holes can occur from pastes which do not allow a full-even print. A paste with a high viscosity is often thought to be the problem source; more likely, a steep slope of viscosity versus shear rate is at fault. That is, viscosity is not responding to shear forces during screen printing. Conversely, a paste with a low viscosity may produce poor grid line quality (line width and definition), not because of absolute viscosity, but because of a flat or shallow slope. This type of paste does not freeze, or set up, quickly enough after deposit onto the silicon.

A. Particle Considerations: Figures 1, 8 and 9 show a variety of silver powders with different sizes and shapes, including finely divided sponge (B), flake (A, C and E), spherical (F), random shapes (D) and random particles with some flake (G). A comparison of particle size distribution curves, weight percent versus equivalent spherical diameter, are shown in Figures 2 and 3 for some of these powders. Volume populations are shown in Figures 4 and 5. The average particle size is important, but differential volume along with particle shape and agglomeration tendencies (revealed in the SEMs) is essential information in selecting the screening vehicle and making rheological adjustments to the paste.

The particle size and differential volume of glass powder, a minor but very important component in silver metallization for application on silicon cells, can be changed by varying the processing time for particle reduction. This is illustrated in Figures 6 and 7. A change in glass particle size will influence adhesion as well as paste rheology. Interestingly, glass particles of optimum size had nearly an ideal, bell shaped population.

B. Particle Effects in Pastes: Silver particles were also characterized from pastes in dried screen prints and sintered (fired) films as shown in Figure 8 for one silver type. Powder clusters, or agglomerates, tended to separate during milling of the paste, revealing truer spherical particle shapes in the dried prints. The spheres tended to retain their shapes in sintered films. Variations in powder lots for the same type of silver are not uncommon. Figure 9 reveals the effects of inadvertent particle size change for silver flake. The acceptable lot (left side) had smaller and fewer large flakes than the unacceptable lot (right side). This is verified by the volume populations in Figure 4. While paste processing tended to fracture and compact flakes from the acceptable lot, the larger and probably thicker flakes in the unacceptable lot retained these characteristics in the dried and sintered films.

C. Paste Viscosity and Slope: The viscosity of a liquid is influenced by a number of extraneous factors, not the least of which is shear force. The response of a thick film paste to shear was shown to have far greater meaning than nominal viscosity. A nominal viscosity can be virtually meaningless if the

slope, or rate of change in viscosity with change in shear rate, is not acceptable. This is illustrated for silver pastes made with Lots C, E and F powders (Figures 10 and 11). The viscosity at a shear rate of  $9.6 \text{ seconds}^{-1}$  for these pastes is nearly the same at 550-600 poise. The viscosity slopes, however, differ from -0.450 to -0.770. Only the slope from paste made with Lot C powders meets a preferred specification from about -0.550 to -0.650. Of the seven silver powder types investigated, pastes from two lots, A and C, met slope specifications. A paste with a slope below this range tended to give poor line definition, lacking recovery capabilities to prevent slumping and moving as it was deposited onto the substrate during screen printing. A paste with a slope above this range tended to lack the necessary flow characteristic to give a full, even print. This condition caused the paste to skip or pin hole during printing. It was theorized that intimate contact of silver particles with the textured surface of crystalline silicon could be inhibited during printing if improper paste flow occurred. Mesh marks were also a product of paste with a steep slope.

D. Paste Adjustment: A lower viscosity at a given shear rate may be achieved by a paste user by adding thinner. This will lower the solids percent, reduce silver content and can lead to electrical and soldering difficulties. While a lower apparent viscosity may be achieved with thinner, a steep slope with attendant printing problems can still persist. Large thinner additions can lower the viscosity slope but cause printed lines to sag or spread. Figure 12 illustrates the adjustment of a paste with an abnormal-high slope (-0.863) by blending in 50% of a paste which contained the same silver powders (Type B) and identical solids; i.e., 80%. This adjusted paste had a slope of -0.548. An "ideal" slope (-0.641) was achieved with the blend of pastes while maintaining the desired inorganic solids content. The viscosity of all three pastes at a shear rate of  $9.6 \text{ sec.}^{-1}$ , the shear rate used when quoting viscosity to the user, was nearly identical at 1000 poise. It was demonstrated from this phase of the study that any number of alterations to the slope could be made to achieve optimum printing performance. Only the organic vehicle was changed to accommodate the characteristics of the silver particles.

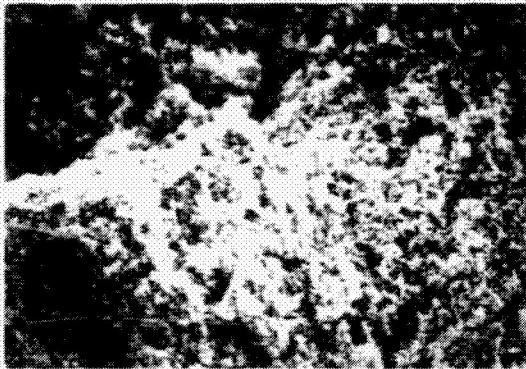
E. Tap Density: A correlation of powder tap density with the slope of viscosity for silver pastes is shown in Figure 13. As tap density increases the slope of viscosity decreases. There was no apparent correlation between tap density and viscosity measured at a single shear rate.

## VI. SUMMARY AND CONCLUSIONS

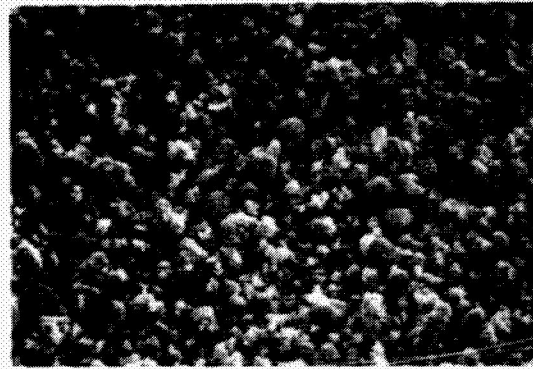
Particles from a variety of silver powders were investigated by scanning electron microscopy and particle size analyses. Particle size distribution curves and volume population graphs were prepared for these silver powders and for glass powders with optimum, extra fine and coarse particle sizes. The viscosity at a given shear rate and slope of viscosity over a range of shear rates were determined for thick film pastes made with these powders. Because of particle anomalies and variations, the need for flexibility to achieve the best printing qualities for silver pastes was evident. It was established that print quality, dried and fired film density and optimum contact of silver particles with silicon, important for cell electrical output, could be achieved by adjusting the slope of viscosity that fell outside of the range, -0.550 to -0.650. This was accomplished through organic vehicle technology that permitted a change in the slope of viscosity, up or down, while maintaining a constant silver and total solids content.

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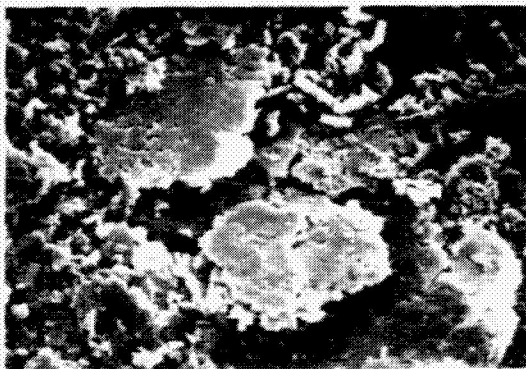
Figure 1. Various Powders Used in Silver Pastes



Type B



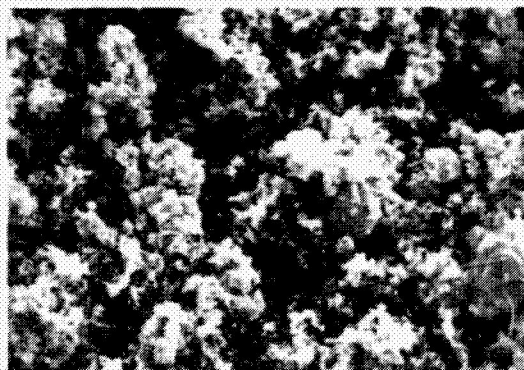
Type D



Type C



Type E



Type G

10  $\mu$ m

Figure 2. Particle-Size Distribution Curves:  
Silver Powders

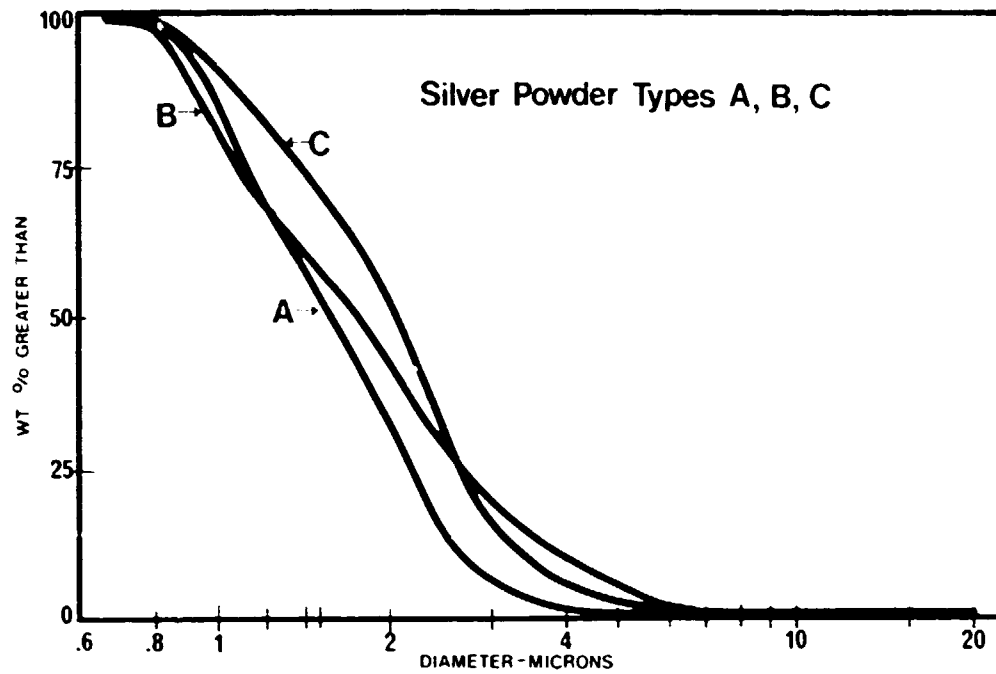
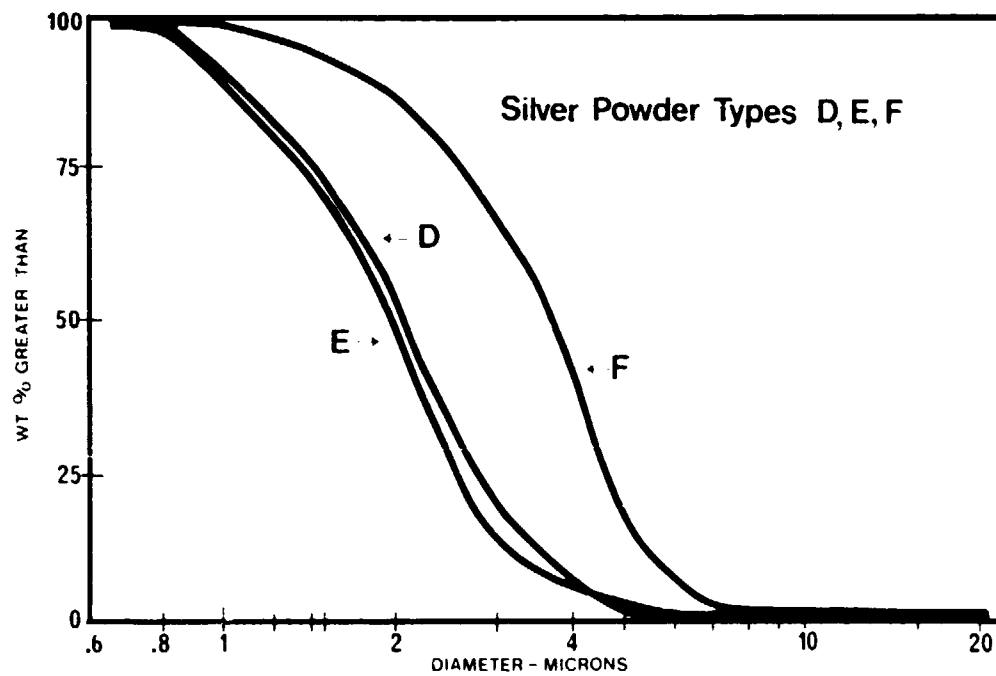
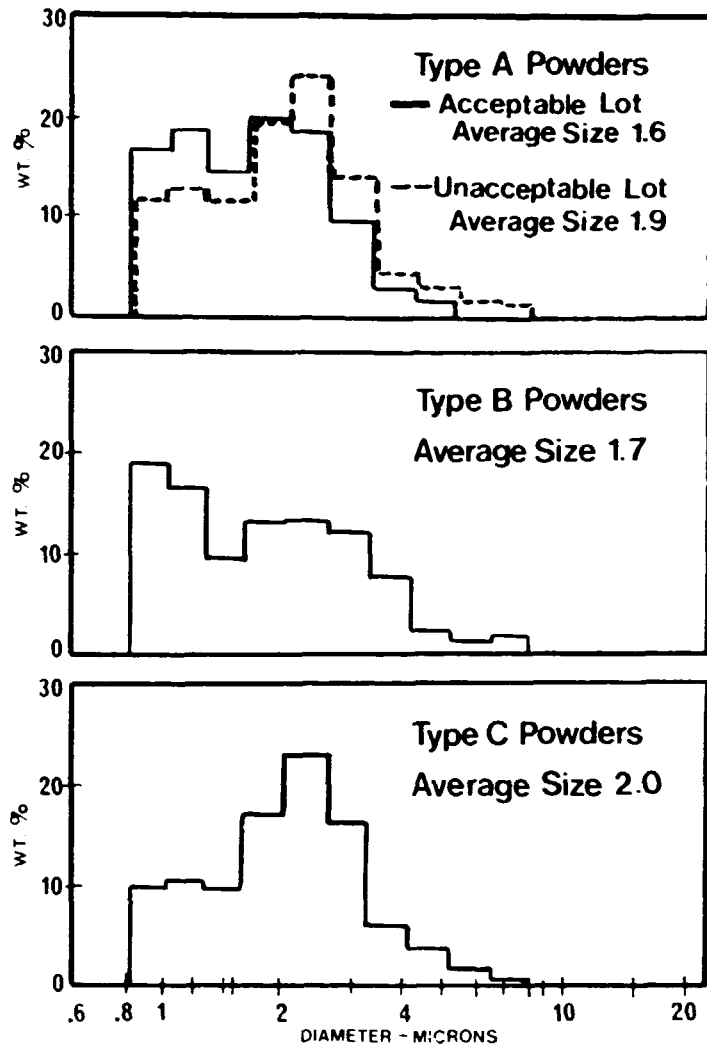


Figure 3. Particle-Size Distribution Curves:  
Silver Powders (Cont'd)



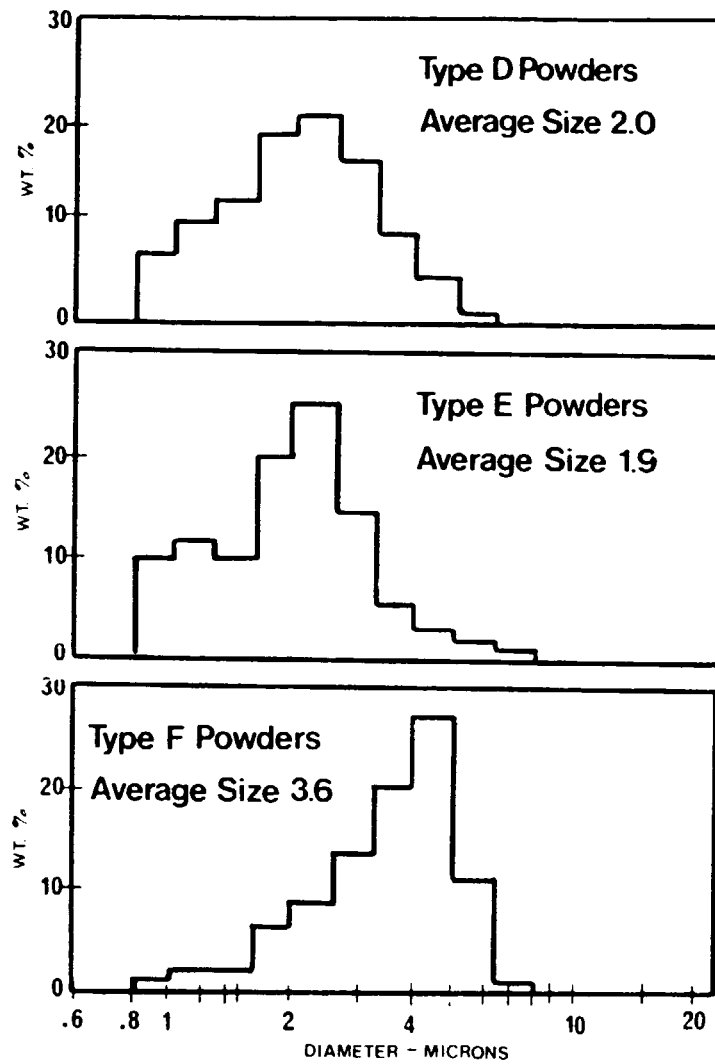
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Figure 4. Particle Size of Silver Powders:  
Differential Volume



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Figure 5. Particle Size of Silver Powders:  
Differential Volume (Cont'd)



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Figure 6. Particle Size Distribution Curves:  
Glass Powders

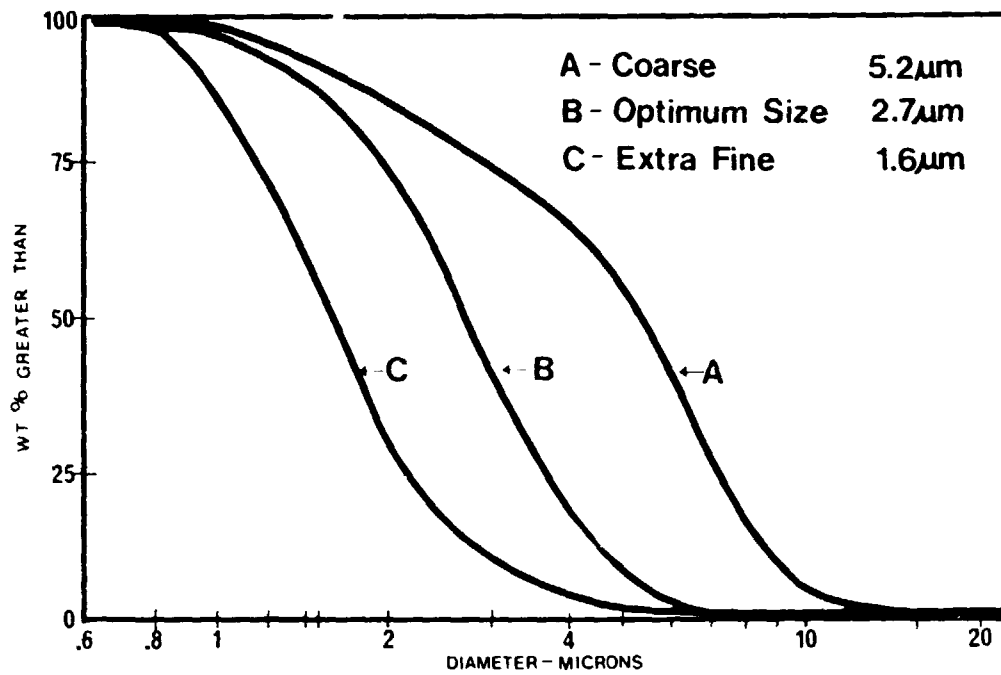




Figure 7. Particle Size of Glass Powders:  
Differential Volume

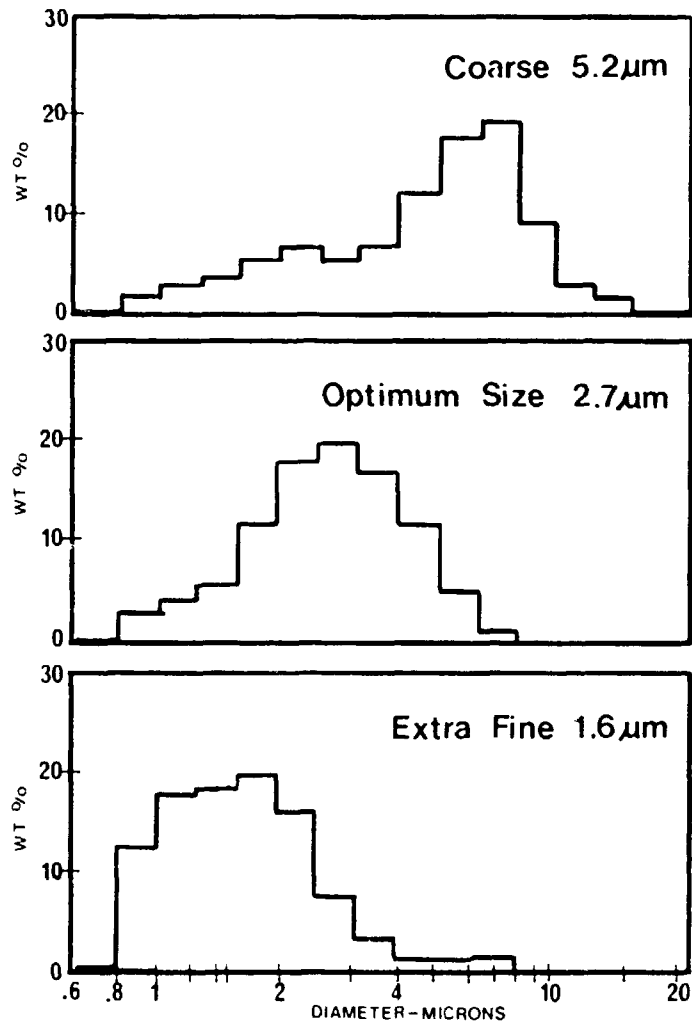
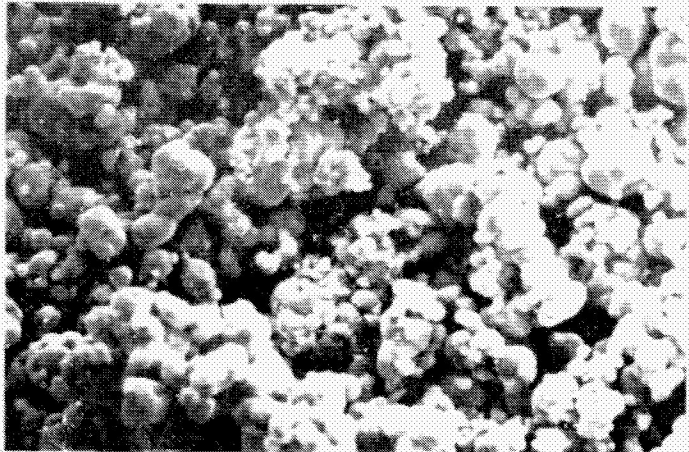
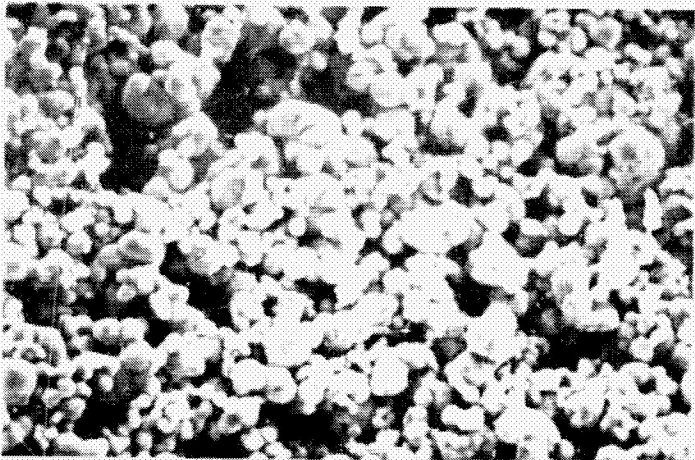


Figure 8. Comparison of Spherical Silver Type F Powder, Dried Print and Sintered Film

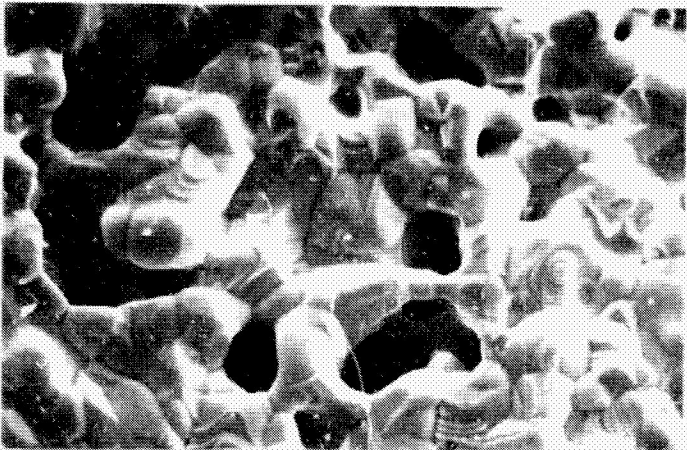


**Powder**

10µm



**Dried Print**



**Sintered Film**

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Figure 9. Comparison of Type A Silver Powders,  
Dried Prints and Sintered Films

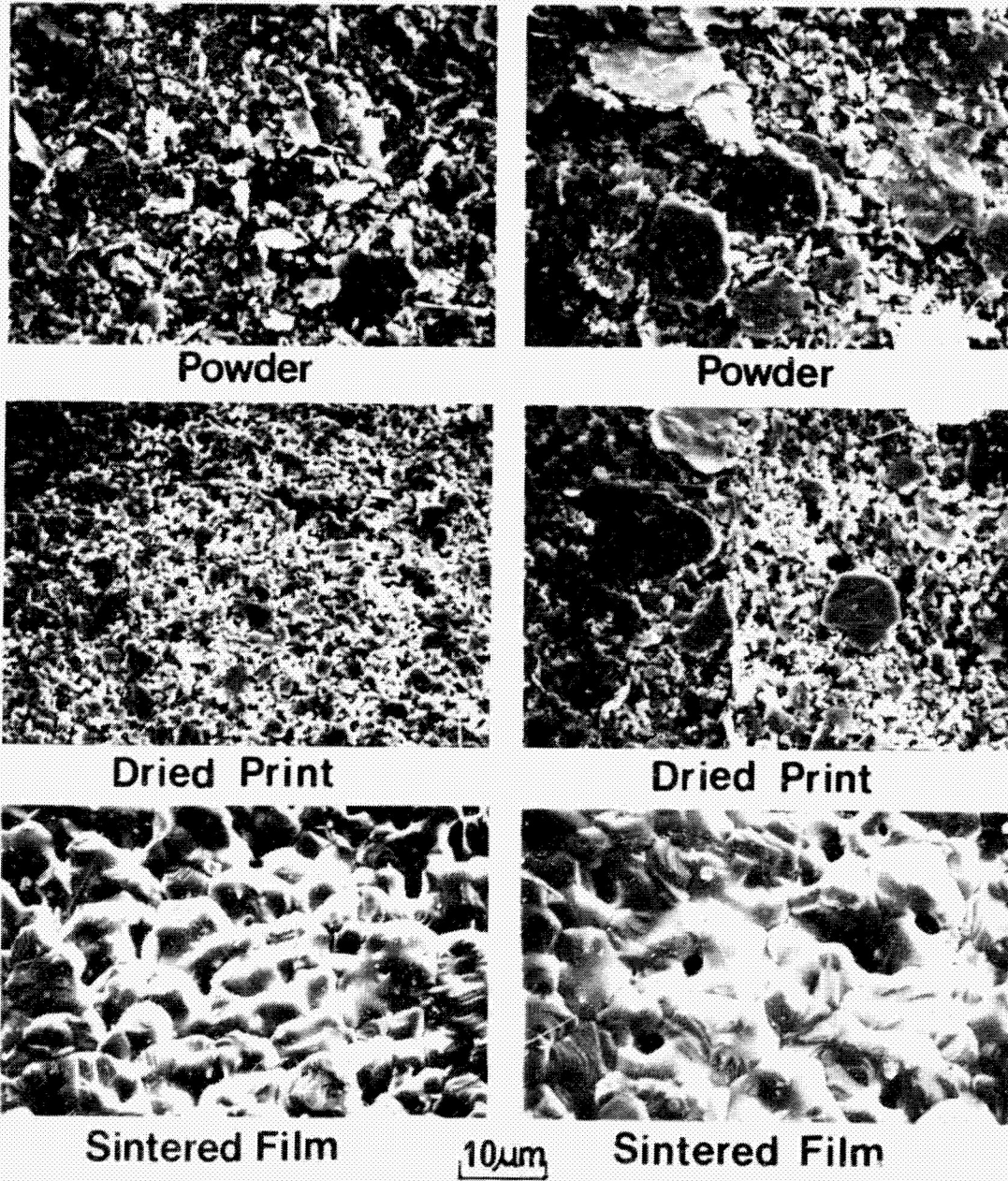


Figure 10. Viscosity: Silver Pastes

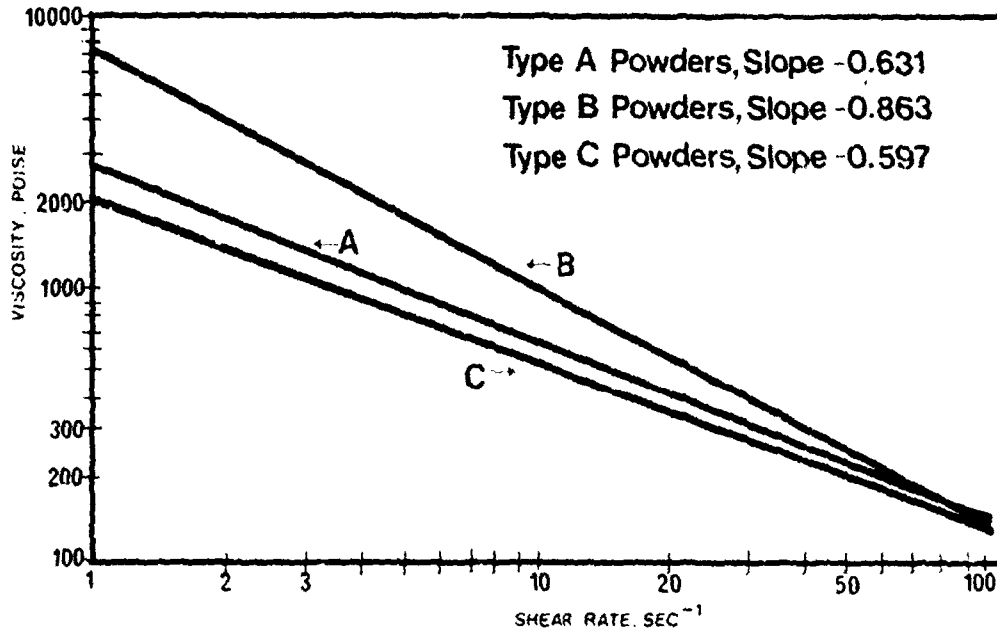


Figure 11. Viscosity: Silver Pastes (Cont'd)

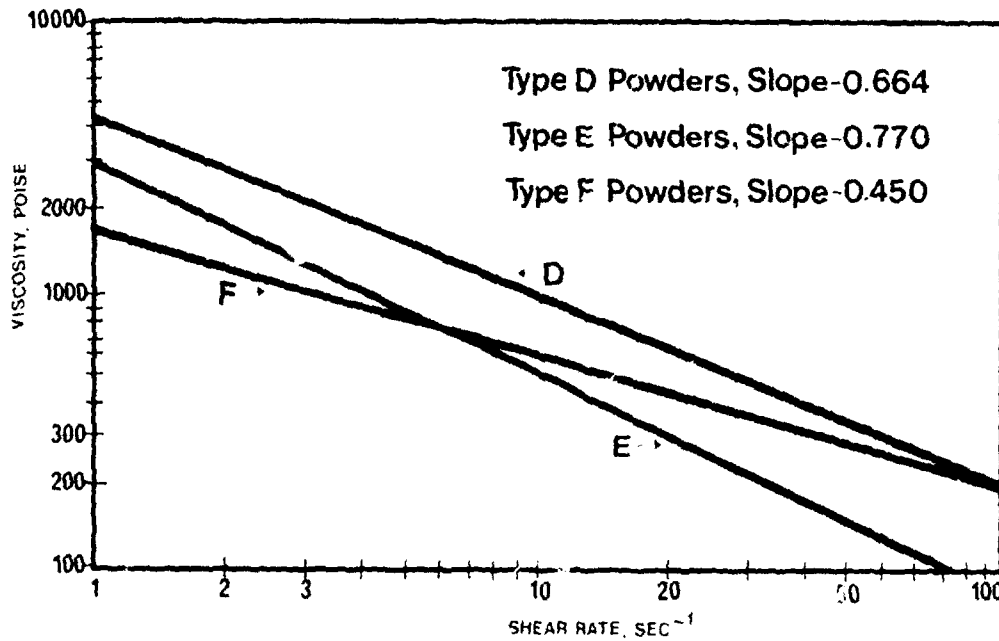


Figure 12. Adjustment of Viscosity Slope  
for Abnormal Silver Paste

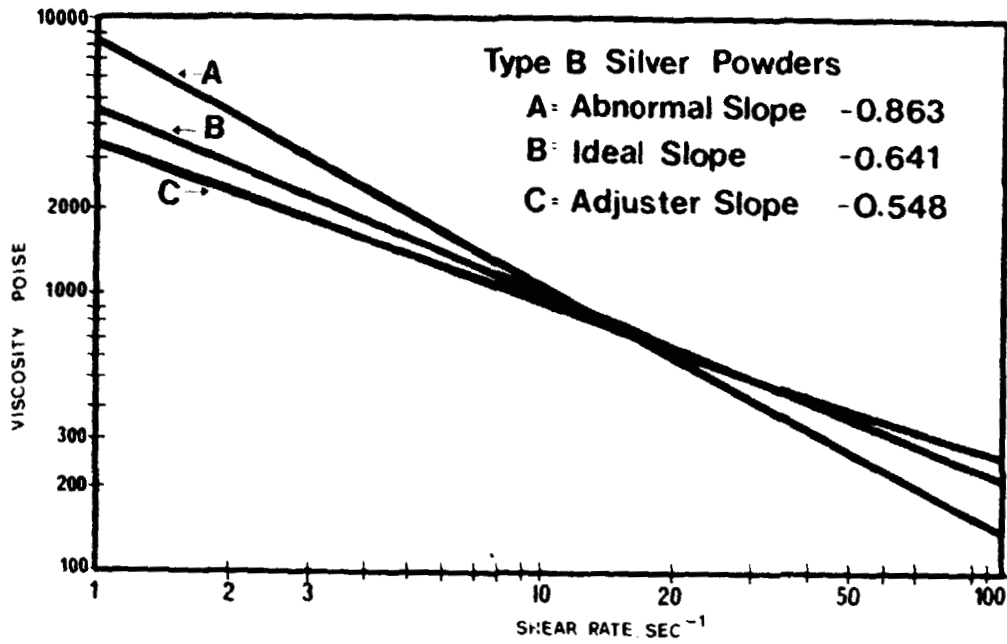
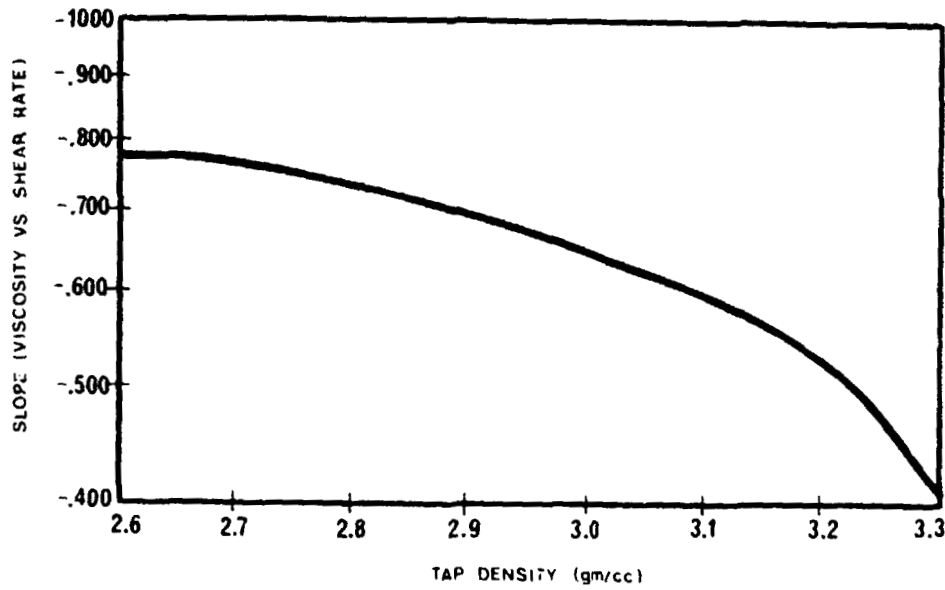


Figure 13. Relationship of Silver Powder Tap  
Density With Paste Viscosity Slope



## DISCUSSION

SCHRODER: When I think of a metal semiconductor contact, I think of a physical contact, even though the electrical contact may only be an electrical or a physical contact. But the physical contact I think of at least is uniform. Now you showed SEM pictures; if you imagined looking at the interface now of that paste and the silicon, what fraction do you think of a given area is physical contact, never mind electrical contact? Would you kind of guess at that? I know you can't look at it.

PROVANCE: Well, it is strictly one where you have to theorize a bit. You can see what is happening on the top and you sort of flip-flop it over and say is this happening on the bottom, and you have to assume that yes, to some extent, it is. If on top you see a lot of irregular-shaped mountains, peaks, and valleys, then you have to assume that the same thing, to perhaps a lesser extent, is happening on the bottom. The degree of physical contact, I wouldn't want to hazard a guess, I'm not really sure, but in theory the more compact the particles are and the more these particles are separated, and deagglomerated, the greater the contact would be.

GALLAGHER: If I may add to that: in the silver system, you can etch the silver away and you end up with the glass. You can look at that, and we have done it on a Spectrolab contract. One thing you are really not sure of, however, is that glass touching the surface, but you can end up with the footprint of the glass.

QUESTION: What did you see?

GALLAGHER: Depending upon the composition of the structure, and the amount of glass that is added to it, you can see great differences in -- I have two gentlemen here who saw the same SEM pictures that I did. They were taken by Ferro, by the way, and I would guess over 30% to 40% of the area at the most was glass, the rest metal.

QUESTION: Was it physically contacted?

GALLAGHER: It was physically contacted.

QUESTION: And then the electrical maybe even less?

GALLAGHER: I have no idea. We at that particular time formulated some structures that had 5%, 10% and 15% of the total weight as glass.

PROVANCE: The glass plays two roles, or at least two roles. One, of course, is to achieve the adhesion, and the second thing, which is often overlooked, is that glass really is an aid to sintering, within a certain amount of glass. In other words, too much or not enough and you can have problems. There is the thing of optimizing just the right amount of glass and the right formulation of glass for that particular task.



HOGAN: We have done pretty much the same kind of thing, looking at the series resistance associated with glass content, metal content and other things, using the same technique or perhaps the same technique, which is a mercury amalgamation where you can remove that silver. We have discovered, not quite that high, more in the range of 20% to 30%, areas that are not glass-covered between the contacts. That does not mean that the silver is even physically, much less electrically, in contact with that area. It is really hard to say what the electrical coverage is. The interesting thing is, we did some HF etching in experimental work and found that improvements were entirely associated with the etch, so that although there is a dendritic nature to the structure, the majority of the improvement was due to an etching along the edges of the contact -- thereby, we assumed, increasing the silver contact there, the electrical contact. It brings up a point I wanted to make: I think a very important study has to be made with this interfacial area between silicon and the thick-film inks. Contrary to many microelectronics applications, where you are putting it on an aluminum substrate, you are not concerned very much about what the electrical properties are between the substrate and the metal, but here we are very concerned about those kinds of things. The question I had, though, was what percentage of the manufacturers do you feel are doctoring the inks, you know, when you were talking about communications? Is that a problem for manufacturers of the ink products?

PROVANCE: Do you mean which ones do and which ones don't?

HOGAN: Yes.

PROVANCE: I don't know which ones will admit it but I will tell you right now that there is no one in business today making thick-film formulations that don't have some way of making these materials behave. The lesser of the two evils is, don't change the inorganic composition, change the organic part, the part that burns out, and make these materials behave, particularly that slope. Anyone that is not doing that would have an awful problem out in the field because, as I say, these powders are somewhat like fingerprints. No two sets are identical. You can make them pretty close, but you are going to have variations from time to time, and I don't think there is any way of determining if they were absolutely identical. The same number of particles, the same shape, same size, same volume population, you wouldn't know it. In other words, there is no way of defining that precisely, whether you have the exact same number of particles at a given size. So I would say that everyone has his methods of making these materials behave out in the field.

GALLAGHER: How did you designate these powders as A, B, C and D?

PROVANCE: Those are internal designations that we use.

GALLAGHER: But what did you use as your criteria for saying this is powder A, B or C? Are they all made the same way and they came out --

PROVANCE: It was sort of which one came through the door first. That was A and B. There was no rhyme or reason, we simply gave them a letter designation for purposes of identifying them.

GALLAGHER: But they were supposedly made the same way and they were supposed to have the same characteristics?

PROVANCE: Yes, of a given type. The letter number designated the different type --

GALLAGHER: I meant E was supposedly made the same as B, supposedly made the same as C -- they were all spheres?

PROVANCE: Oh, no. A, B, C, D, E, F and G were all different types of powders but we showed one example, supposedly the same type of material from two different lots, and found that indeed they weren't the same. We find that with whatever letter it was or whatever type of silver, the materials do change from lot to lot. Sometimes dramatically, sometimes a little bit but always enough to change, if not absolute viscosity at one shear rate, the slope of viscosity. And that is what we put the emphasis on in trying to adjust that slope back so that the materials will handle the same on a screen printer.

R. VEST: The question was asked a little earlier about how much metal is in contact. That's really not a good question, because it depends on the processing. If you have a printed conductor such as we are talking about here, the amount of glass that is in contact with the substrate as opposed to how high a temperature and how long you fire it -- in general, if you fire high enough and long enough, you will end up with a continuous glass film under the conductor, so you have no metal contact with the substrate. So this is another question that you have to ask: not only how much is in contact, but how much is in contact when we process this particular ink at this temperature for this time. Then it is a reasonable question.

I have one other question. In addition to your slope, you also pick a value at 9.6. I didn't catch what that value was, and why did you pick 9.6?

PROVANCE: That happens to be the mid-point of the five shear rates that we used, and it was simply a matter of convenience. That is what we show in our literature. Almost all thick-film paste manufacturers have a viscosity specification, and it obviously has to be taken at one shear rate. As a matter of convenience, we picked the midpoint of the five that we used, and quote that in our literature. I am the first to admit that that number can be very misleading if you don't have the entire picture of what happens when you shear the material.

R. VEST: What is the range you shoot for at 9.6?

PROVANCE: In the case of conductor pastes, it varies per application and type of metal. In the example I will use, if you are going to go a large screen, such as in the use of making optoelectronic displays, gas-discharge displays, the customer works with large sheets of glass. We found from experience that the squeegee material that pushes the paste through the screen is going to be different than it is on a smaller screen. In microelectronics, most of our pastes are tailored to a relatively small screen, 12-inch-square or smaller, for small devices.



But on a large screen, we have found that you need an absolute viscosity of about 600 poise where on a small screen you need more like 900 to 1000 poise. So at midpoint it varies with the application, and quite honestly, the technology in solar cells is considered somewhat secret. Our customers will sometimes communicate back to us and sometimes they won't. More often than not, if they have a printing problem and we are brought in and can see what they are doing, we can correct it simply by adjusting the organic vehicle so it will print regardless of what size screen they are using or what type of squeegee material they are using.

**SOMBERG:** Would you care to comment about this previous point I brought up about the presence of organics in, say, solar-cell firing. Being aware of the fact that it is spike-fired but it does go through a burnout? Other than metal stearates, things like that, would you comment about the presence or absence of organics through that burnout phase, say through 550° to 600°C?

**PROVANCE:** In the early going (ceramics), and in the early going of solar cell manufacture (we are talking about maybe four or five years ago) I was a nonbeliever that you could achieve sintering and maximization of adhesion when you peak fire at 60 to 120 seconds. I saw these reports coming, most of them JPL-sponsored, and I said no way can you make thick film work, because I have been in this business for 20 years and we thought we did a marvelous thing when we came from 980°C down to 850°C and brought the cycle time down from one hour to 25 minutes. I became a believer when we went out into the field to one of our customers and printed some parts and set up -- in fact, we turned the furnace on for them. A strange-looking furnace, this IR furnace, which you turn on like a light bulb; it is unconventional, compared with the standard type of furnace, and within an afternoon I was convinced that there was indeed something to that, because I recall I set up three or four profiles from about 500° to 700°C with different times, and one of the early tests which is still used was simply for adhesion, putting Scotch tape down and pulling it off. Before the afternoon was over, I could see that it was certainly passing the Scotch-tape test and it appeared to be a rather dense film. We subsequently went on to study thick-film resistors. In fact, four weeks ago I was in Dallas giving a talk on properties of thick-film resistors fired in an IR furnace, going from the conventional 25- to 30-minute cycle, down to 4, 5 and 6 minutes, which is still long by solar cell standards but much faster than conventional thick film. I can't disagree with Dr. Stein that there is obviously something trapped in there, but it is a negligible amount, we feel, because resistors, especially, are very sensitive to thick-film processing. In this particular series we developed a TCR (temperature coefficient resistance) of 0 to 40 parts per million, and anything that is not right will offset and create an imbalance so that you can't achieve this. Obviously, we are trapping something when we fire in 60 seconds or 120 seconds. I am not sure that anyone has measured just how much. A rough measure would simply be to take a weight with a fine balance to five or six places and fire it and weigh it again. I am not sure that will clear up the mystery, because that still might not be accurate enough to say just how much is coating those particles. It is pretty difficult to imagine that you are indeed burning out an organic binder in a matter of a couple of minutes. When

you consider the shape of those particles, the little crevices and so many places to have binder trapped in there, it is pretty difficult to imagine that you are burning it out clean. Just how much remains, I don't think we know. That is probably something that should be looked into.

WEAVER: Being a field test engineer and not understanding all of this, I was wondering if you used the glass frit, what would happen if you used, say carbon fiber in there with them, because it is more conductive? Would that be detrimental or beneficial, or it wouldn't make any difference?

PROVANCE: Well the glass frit is used to help the sintering processes as well as adhesion. The fiber might help the electrical properties, but you wouldn't get any adhesion benefit from it, or sintering values.

STEIN: There was a question raised before, I think it was from the man from SERI, about the possible modifications to the inks, and it was interpreted as being modifications that the paste manufacturers could make. I would like to suggest also another kind of modification that we have encountered which is done by the customers, and it is highly secret. But basically, in a number of instances we know that people are throwing all sorts of things into the silver pastes on the solar-cell user side. These can have rather dramatic effects. I will give you an illustration. In Europe, some of our customers used one of our silvers, which fires up in the 830° to 850°C region, and it is a totally different system and they insist they like it a lot better than this low-temperature stuff that might peak-fire at 700° ± 20. We know that they throw in titanium, in one instance, we know that some others throw in tantalum, we know that a number of other things are used. Coming back then to the basic question of what happens at the interface? Is it a glass contact in part and a silver contact in part? There has to be an interaction between the silver and the silicon, there has to be some diffusion to get good electrical contact. There are probably doping effects due to these additives, and there are very likely new compounds formed at the interfaces, so it is a rather complex picture and it is not an easily answered question. We therefore offer a variety of silvers containing, let's call it dopants, or sintering aids. In fact, if anybody wants it, I am sure that Thick Film Systems or Electro Science Labs will custom-make something with any garbage you want put in it, because we don't understand it.

HOGAN: That was really the intent of my question, because I know it is very easy for a silicon-cell manufacturer to add a little liquid boron dopant to the silver ink and think that is going to do something for his contact. It may or may not. I was just wondering what kind of problems you got into as a manufacturer in trying to straighten out somebody's printing problem when Lord only knows what is in your ink after it's gotten into the plant?

PROVANCE: That is a big problem and as Sid (Stein) says, we will make anything anybody wants. Actually, the manufacturer of the thick film formulation is better equipped and better able to do that because the fine tuning of the screening characteristics as well as the electrical properties can best be done by the person that is making this material.

Once the material is out in the field and altered, it may be altered to achieve a certain physical benefit in the screen printing, or some electrical property, but it could be creating other problems. When a customer does alter these materials, it is generally over a period of time and he has also learned to live with altering this and he makes it work, one way or another. What we are saying is, it is very likely that the thick-film paste manufacturer would be able to achieve this in a shorter period of time and guarantee that it would work time and time again.

**AMICK:** Do you have any limits, then, to what you would accept in the way of initial ink? Because you know you can tailor that by making up combinations of different binders and then blending, to come within specifications. Are you saying you don't really have any criteria for the original selection?

**PROVANCE:** Yes. You can live with a certain amount of variation, from time to time, but you can't live with a fired surface that is rough and does not hold line definition. In all cases, all of these powders either experimentally or in production get made into a paste and with full quality control. What we try to do is weed out, as I mentioned earlier, a disaster where you commit several thousand grams of material, or more, to a batch of material only to find that you have made a mistake. You might call it an early warning system. Yes, there are limits as to what we would use. In fact, if the differences between powders are gross, which they were with lot A, shown in the slide, that particular unacceptable lot never make it to manufacturing. What we are looking for is tailoring the small differences, relatively small differences, yet important differences to the slope as well as to the viscosity at a standard shear rate. Yes, there are limits. The use of the vehicle technology, you might say, is a fine-tuning instrument to make the material behave, that misbehaves in the particle state.

**NAZARENKO:** Just to expand on what was just said, we are constrained on the type of vehicles we can use because the materials are selected so that they offer clean burnout. We try to design the materials so there are no residual carbons or other types of impurities left after the burning cycle. Functional groups on the vehicle will dictate how efficiently these materials are going to be burned out. So there are some limits.

**PROVANCE:** These binders do burn out rather rapidly and the principle deterrent to them burning out clean, as Sid Stein said, was the fact that you have to watch that you are not melting the glass or sintering the particles to the extent that you capture and freeze these in. But most of these materials have been well researched down through the last three, four or five years and the organic vehicles are better than what they were eight or 10 or 15 years ago. They do burn out pretty quickly so you can, even in conventional firing, come up rather sharply and burn those materials out in a conventional furnace in seven or eight minutes. The old profiles, and I am talking 10, 12 or 15 years ago, used to come up and level off at 500°C and then come on out just to get rid of the binder. It is no longer necessary to do that.

**AMICK:** Does anyone do microcombustion analysis now to find out how much carbon there is left after binder burnout?

STEIN: We do that.

STEIN: The comment I made earlier was not related to the burning out of the vehicle, which can be handled. It was related to the organics trapped or coated on the surface of the silver particles as Jay (Provance) or anybody else receives them. If they are precipitated particles, precipitated in the presence of a protective colloid, precipitated in the presence of an organic acid with a carboxyl group or precipitated in the presence of some other, heaven forbid, halogenated or sulfonated or other kind of active chemical group. That is very difficult to get rid of and that is present in an extremely minute amount but it can affect the sintering rates. That is what I was talking about.

PROVANCE: That is a very good point, and while I don't want to discuss exactly how we do this, we do make a test for just that sort of thing to keep our suppliers of powders honest, you might say. So we do have some limits on what we will accept in the way of coatings that may or may not be on those particles as we receive them because that can have an overpowering influence on how these materials sinter as well as how our organic vehicles are going to work.