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MOD SILVER METALLIZATION FOR PHOTOVOLTAICS


Purdue Research Foundation

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JPL Flat Plate Solar Array Project

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# FOREWORD

The research described in this report represents the fourth three months of effort on Contract No. 956697 with the Jet Propulsion Laboratory, Pasadena, CA, under the technical cognizance of Brian Gallagher. The research was conducted in the Turner Laboratory for Electroceramics, School of Materials Engineering and School of Electrical Engineering, Purdue University, W. Lafayette, IN under the direction of G.M. Vest and R.W. Vest. The research was carried out by Dr. S. Singaram and Mr. C.J. Sabo with assistance from Mr. R.L. Reed.

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# 1. INTRODUCTION AND OBJECTIVE

Photovoltaic cells require back side metallization and a collector grid system on the front surface. Both front and back surface metallizations should have good adhesion, low contact resistance, low sheet resistance, long term stability, and their deposition methods should not degrade the n-p junction. In addition, the metallization for the collector grid should be capable of producing small grid spacings and grid widths. For the terrestrial flat-plate solar array project, low cost of the metallization is also a very important requirement. One of the dominant systems in use today is screen printed thick film silver conductors. When such conductors are used in hybrid microelectronics they are typically fired at temperatures from $650-850^{\circ}$C for 10-15 minutes, but for solar cells they must be rapidly fired in order to avoid degradation of the junction. This rapid firing compared to the conditions for which the inks were developed often leads to poor adhesion, and porous silver films are always the result. In addition, typical frit bonded thick film silver conductors may present a special problem because the frit dissolves the $SiO_2$ film on the photovoltaics and sometimes produces a reaction layer down to the junction.

Metallo-organic (MO) compounds are ones in which a metal atom is linked to a long chain carbon ligand through a hetero atom such as O, S, N, P or As. In order that the products of decomposition contain only $CO_2$, $H_2O$ and perhaps nitrogen compounds, Purdue's Turner Laboratory pioneered the use of a set of MO compounds for ink fabrication where the linking hetero atom was oxygen. Films produced by the metallo-organic

decomposition (MOD) process have a number of advantages compared to conventional thick films. The approach followed at Purdue will lead to generic inks because all of the compounds used are either purchased as pure materials or synthesized from commonly available reagents. Even if conventional inks did not contain proprietary additives they still could not be duplicated in the user's laboratory because film properties are dependent on characteristics of the particulates (average particle size, particle size distribution, particle shape, etc.) in addition to their chemical composition. All chemical compounds are in solution in inks for the MOD process, which means the mixing of the constituents is achieved on an atomic scale, and films produced after decomposition of the organic compounds reflect this uniformity. The uniformity of conventional thick films is a strong function of the degree of blending of the particulates in the organic screening agents, and there is always an inherent nonuniformity due to the finite particle sizes of the different constituents in the inks. Films produced by the MOD process are inherently thinner than films produced by conventional thick film technology because the volume change from wet to fired MOD film is typically a factor of 50 compared to a factor of 3 for conventional thick films. This can be a disadvantage if very high conductance is required, but can partially be overcome by deposition of thicker films or multi-layer films.

MOD silver films have the potential for eliminating most of the present problems with silver conductors. Preliminary results indicate that the MOD silver films can be produced at much lower firing temperatures (e.g. $300^{\circ}$C), which should reduce chemical interaction effects as

well as deterimental thermal effects on the junction. The specific technological objectives of the current program are to identify and characterize suitable MO compounds, develop generic synthesis procedures for the MO compounds, develop generic fabrication procedures for screen printable MOD silver inks, and optimize processing conditions to produce grid patterns on photovoltaic cells. The metallizations will be evaluated as to their appearance, line definition, adhesion, sheet resistance and microstructure. The metallized cells will be evaluated at JPL as to their performance as solar cells. Once a suitable MOD silver ink or inks has been developed a small weight percent ($<5$ w/o) of a suitable platinum MOD will be added to give the ink good solder leach resistance which silver films alone do not possess. The platinum addition will also allow for quantitative adhesion data to be collected. The silver/platinum metallizations will be evaluated on the same criteria as the silver metallizations. The adhesion and sheet resistance will also be evaluated after thermal aging. Another objective of the program is to develop a model which describes the adhesion between the MOD silver/platinum film and the silicon surface.


## 2. SUMMARY


Major areas of the metallization process were examined in order to determine whether or not a major ink chemistry change could be avoided by making relatively minor changes in the processing in order to give consistent excellent initial adhesion and long term adhesion. All results suggested that the adhesion strength is very sensitive to the ink and its processing. It was also learned that the difference in

surface roughness between alkali and acid etched solar cells does not have a significant effect on resulting film adhesion. In order to overcome the effects on adhesion of minor variations in the metallization process, a permanent binding agent in the form of a MOD compound was sought. Bismuth 2-ethylhexanoate proved to be suitable MOD compound which would impart consistent initial as well as long term adhesion by decomposing to bismuth oxide in the fired films. The presence of bismuth oxide has significant deterimental effects of on film sheet resistance such that multi-layer films will be more necessary than before. Finally, the processing of multi-layer films has presented some problems with film stability as multi-layer fired films have shown considerable cracking which destroys adhesion.

## 3.  REVIEW AND APPROACH

### 3.1  General

During the last weeks of the previous quarter it became obvious that silver/platinum ink SPC1-YZ was not a viable conductor ink for photovoltaic cell metallization from a long term adhesion standpoint. In addition, films printed with ink SPC1-YZ were beginning to show inconsistent initial adhesion results as well. Two different approaches were undertaken during this quarter, although both had the same basic goal. The first involved studying various aspects of the processing of ink SPC1-YZ in order to determine if relatively simple processing adjustments would be made to improve both initial and long term adhesion. The other approach began about one third into the quarter after it appeared

that simple processing adjustments alone would not solve the adhesion problem. This approach involved the selection of a suitable binding agent in the form of a metallo-organic compound as a permanent addition to the ink. Together, these two approaches will hopefully produce both a better understanding of the adhesion mechanisms of silver/platinum films from MOD inks to silicon solar cells and consistent initial and long term adhesion results also.

## 3.2  Possible Explanations for the Loss of Initial Adhesion

Once the problem with obtaining consistent excellent adhesion results as well as any significant long term film adhesion was noticed, a complete evaluation of the entire metallization process was undertaken. It was hoped that such an evaluation might lead to information which would allow for minor processing adjustments to be made in order to improve both initial and long term film adhesion. Such a solution to the problem is certainly more attractive than making major changes with the processing of the ink or its chemistry. Three major areas of cell metallization were studied: the solar cell surface roughness; the ink formulation; and the thermal processing of the printed films.

Substrate surface roughness can have a considerable effect on film adhesion. Generally, rougher surfaces provide a better interface for film adhesion as long as they are not too rough so as to prevent proper printing, complete substrate wetting and acceptable line definition. During the course of this project, solar cells were provided by JPL with two different surface roughnesses due to a change in etchants used to remove damage on the cells after sawing. Prior to July 29, 1984 all

printing and firing was done on the rougher alkali etched solar cells (batches 172-2 and 341-177). This includes all inks through the 5th printing of batch 2 of SPC1-YZ with the exception of SPC1-2D. After this time the somewhat smoother acid etched cells were used (batches 346-193 and 346-199). Because of this difference in surface roughness and the fact that the problem of less than excellent initial adhesion was first noticed for the smoother cells, an investigation into the relationship between solar cell surface roughness and resulting adhesion was warrented. Unfortunately, there were no virgin alkali etched cells available for such a comparison. This necessitated the use of a reclamation process by soaking "used" cells in 15% nitric acid in water. Since nitric acid does not attack the silicon surface this type of process allows for removal of the fired films without affecting the surface roughness.

A second possible cause for the sudden lack of excellent initial adhesion for films printed with ink SPC1-YZ may be connected to the particular batch of ink in use at the time. When the proper firing sequence was used (e.g. std. firing sequence #1) and with the exception of the very first single and double layer films printed, ink SPC1-YZ had given films with consistently excellent initial adhesion until a third batch was used. The initial adhesion problems first surfaced once this third batch was put into use. Possible problems with the ink include impurities in the new batch of silver neodecanoate which was used to make batch 3 of SPC1-YZ, a shelf life problem with the platinum 2-ethylhexanoate, or other unknown impurities introduced during the formulation process. The best way to check out the possibility of the adhe-

sion problems being connected to the particular batch of ink is to care-
fully formulate a fourth batch of ink from completely fresh ingredients
and print and fire some films with it to see if the initial adhesion
problems persist.

The last area to be investigated is the processing of the printed
films themselves in order to see if some irregularity was present during
processing which might have led to the adhesion problems. This area is
the most difficult to investigate since the atmospheric conditions in
the laboratory are not monitored with the exception of humidity and tem-
perature and neither of these were abnormal during the processing of the
batch 3 films which showed less than excellent initial adhesion. Since
the complete metallization process from ink formulation through film
firing is not carried out in a clean room environment, it is always pos-
sible that impurities may be introduced which can cause poor quality
fired films. As an example, it is known that the presence of chlorine
has disastrous effects on resulting thick film resistor properties.
There may be a similar type of impurity which can result in a adhesion
losses in thick film conductors although such a possibility is specula-
tive at best. Besides conditions in the atmosphere, the profile in the
belt kiln was checked even though the furnace settings were the same
once standard firing sequence #1 had been implemented. Also connected
to the firing is film thickness since films of different thicknesses may
require different firing parameters. The ink formulation and screen
printing are carried out in the same way each time in order to insure as
constant a film thickness as possible. The dried film thicknesses are
also monitored as closely as possible in order to locate any films which

may have considerably different thicknesses from normal single layer films.

## 3.3  Necessity of Permanent Binding Agent

It became apparent from processing studies conducted late in the third quarter and early in this fourth quarter that the mechanism responsible for silver/platinum film adhesion to silicon solar cells is very sensitive to processing. Even if the proper processing is used to give excellent initial adhesion, studies during the third quarter showed that this adhesion begins to degrade within one week. Due to the necessity of a 30 year lifetime for terrestrial solar cells under the specifications of the JPL Flat Plate Solar Array Project, these results are clearly unacceptable. Although a poorly adhering collector grid would continue to collect current from the solar cell, the corresponding high contact resistance would lead to very poor efficiencies for the light to energy conversion. It is therefore very important to have a collector grid which will maintain strong adherence to the solar cell for the entire lifetime of the cell.

As mentioned in the previous section, the first approach was to investigate the complete metallization by MOD process to see if a relatively simple change in procedure or processing could considerably increase the long term adhesion, not to mention giving consistently excellent initial adhesion as well. Although this approach could still theoretically give the desired results, it is not a practical approach from the standpoint of time as the most obvious processing areas were found not to be major contributors to the poor adhesion results. The

second approach was therefore to select a suitable binding agent as a permanent addition to the ink to promote long term adhesion. Although this change in chemistry may lead to several necessary changes in processing, the potential advantages in terms of obtaining long term adhesion in the shortest amount of time, should easily outweigh any disadvantages associated with this chemistry change.

## 4. EXPERIMENTAL

### 4.1 Ink Development

#### 4.1.1 Selection of Appropriate Permanent Binding Agent

There are several major considerations involved in the selection of a permanent binding agent. There are essentially four types of binders used in thick film systems. These are frit or glass bonders, flux bonders, reactive bonders and mixed (combinations of the first three) bonders. As discussed in the first quarterly report, silicon and boron metallo-organic compounds were tried as frit bonders with the silver neodecanoate. It was hoped that these would form some glass in the film which could react with the $SiO_2$ monolayer present on all silicon surfaces to give adhesion. Unfortunately, the result was black/brown nonconducting films. Frit bonding is still a possibility, but improved Si and B compounds would have to be developed. Flux bonders rely on the formation of a liquid when at least one constituent in the ink melts during firing. Base metal oxides (e.g. $Bi_2O_3$) are commonly used as flux bonders in thick film conductors such as gold and silver, but they must

be fired above the melting point of $Bi_2O_3$ (820$^{\circ}$C). The low firing temperature (<300$^{\circ}$C) used in the silver MOD system eliminates flux bonders from consideration. Reactive bonders are used only with alumina substrates and therefore are of no concern for this project, and mixed bonders would be ineffective based on the above discussion.

In order to find a suitable bonder for the silver MOD system some other adhesion technology must be applied. The technology tried first was actually a thin film one which widely governs the selection of bonders when thin films are being deposited. The basic principle involves one of the few good correlations which exists as far as adhesion is concerned. It is known that the higher the free energy of formation that a given metal's oxide has, the better the metal's adhesion will be. Therefore, gold and silver tend to have poor adhesion while chromium and nickel tend to have excellent adhesion. Although the current metallization research deals with a thick film technology the resulting fired film thicknesses (usually between .5 and .8 μm for single layer films) approach those normally associated only with thin film technology. Therefore, this widely used thin film adhesion correlation was believed to have potential application in the silver MOD system. In order to apply this correlation, two important factors must be considered. First of all, any oxide considered must be able to be formed from an easily obtainable and well characterized metallo-organic compound. Secondly, this compound, once selected, must decompose to the oxide in air at a temperature low enough so as not to disrupt the silver or silver/platinum films which form by 250$^{\circ}$C and 310$^{\circ}$C, respectively. Other minor but nonetheless important considerations for the bonding

compound are similar to those which were applied in the selection of a suitable platinum compound. These are:

1. The MOD compound should not react with silver neodecanoate or platinum 2-ethylhexanoate (no precipitates should form).

2. The MOD compounds should not contain sulfur or halogens since these will result in the production of toxic vapors during decomposition, nor should they contain any sodium or potassium since these ions may migrate into the silicon and degrade the cell performance.

3. The compounds must be soluble in at least one organic solvent which also dissolves the solid silver neodecanoate and is mutually soluble with the viscous, liquid platinum 2-ethylhexanoate.

4. After solvent removal, the ink should be a smooth homogeneous paste and should not contain particles.

These considerations essentially limited the best choices among the currently developed MOD compounds to two: copper 2-ethylhexanoate and bismuth 2-ethylhexanate. The copper compound was immediately eliminated since JPL research has shown that copper severely degrades the lifetime of solar cells when it is present in the metallization. This leaves the best choice as the bismuth compound. Although bismuth oxide's free energy of formation is not as high as chromium's or nickel's it is much better than that of gold or silver. It was therefore decided to use bismuth 2-ethylhexanoate in the ink in an attempt to promote long term adhesion.

## 4.1.2 Synthesis and Characterization of Bismuth 2-Ethylhexanoate

Reaction:

$$C_7H_{15}COOH + NH_4OH \rightarrow C_7H_{15}COONH_4 + H_2O$$

$$Bi(NO_3)_3 \cdot 5H_2O + 3C_7H_{15}COONH_4 \rightarrow Bi(C_7H_{15}COO)_3 +$$

$$3NH_4NO_3 + 5H_2O$$
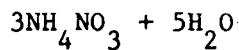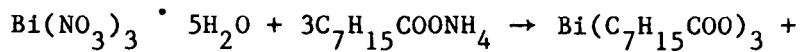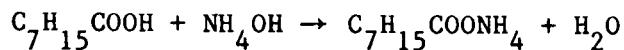
Bismuth nitrate (15 g = 0.0309 moles) was dissolved in 10% aqueous nitric acid (30 ml contains 4.26 g $HNO_3$ = 0.0676 moles) to give a clear solution. In a separate beaker containing a bar magnet, 2-ethylhexanoic acid (26.73 g = 0.1854 moles), 58% ammonium hydroxide (15.27 g = 0.2530 moles) and water (75 ml) were mixed together. The bismuth nitrate solution was then slowly added to this ammonium 2-ethylhexanoate solution. At the end of the addition, a white oil separated and stirring was continued for 30 minutes. This white oil was then extracted in 40 ml of benzene and dried over molecular sieves to remove any moisture.

This compound is liquid with a theoretical bismuth content of 32.74 w/o. A benzene solution of the bismuth 2-ethylhexanoate was subjected to thermogravimetric analysis (TGA). At a heating rate of $10^\circ$C/minute, the TGA showed complete carbon removal by $340^\circ$C and a 14.4 w/o $Bi_2O_3$ content.

## 4.1.3  Ink Formulation

The next step following the selection and synthesis of bismuth 2-ethylhexanoate was to incorporate it into the ink formulation procedure. An initial choice of a 5 w/o bismuth addition in the form of bismuth oxide was made because this is a typical amount used in flux bonded conductors. In gold MOD inks formulated in the Turner Laboratory bismuth additions were typically in the 0.5 to 2.5 w/o range. The choice of 5 w/o in the silver-platinum MOD ink should allow for a clear evaluation of bismuth oxide´s effectiveness as an adhesion promoter. As with any addition to the ink, a minimum amount will eventually have to be determined since bismuth oxide is expected to severely degrade the resistivity of the silver or silver-platinum films.

Using the information from the thermogravimetric analysis of the bismuth 2-ethylhexanoate in benzene solution, the amount of the compound necessary to give 5 w/o bismuth in the ink was determined. This was combined with appropriate amounts of silver neodecanoate and platinum 2-ethylhexanoate such that the remaining 95% of the fired film would be 91 w/o Ag and 4 w/o Pt. The addition of the bismuth 2-ethylhexanoate should not significantly change the ink rheology so the amounts of screening agent used for ink SPC1-YZ were unchanged. These amounts were: NDA (neodecanoic acid) as 26 w/o of the solid silver neodecanoate; and BCA (butyl carbitol acetate) as 13 w/o of the solid silver neodecanoate.

The resulting ink with the bismuth 2-ethylhexanoate addition was very screen printable and appeared very homogeneous. Thermogravimetric

analysis on a sample of the ink at a heating rate of $10^{o}$C/minute showed complete carbon removal by $315^{o}$C, which is not significantly higher than the $310^{o}$C found for silver-platinum inks. Early studies with the ink indicate that it also possesses good stability on the screen during printing as well as long term stability in terms of its ability to maintain a moist, screen-printable texture during storage. This ink will be coded ink SPC2-YZ where Y is the batch number and Z refers to the number of the printing (A, B, C, etc.).

## 4.2 Processing of Films Made from Ink SPC2-YZ

Since previous research did not reveal any problems with obtaining fired silver-platinum films from ink SPC1-YZ by standard firing sequence #1 (with the exception of long term adhesion), this same firing sequence will be employed for films printed with ink SPC2-YZ. Standard firing sequence #1 involves 30 minute batch drying at $65^{o}$C followed by belt furnace firing according to the profile shown in Fig. 1. Unless this sequence does not allow proper decomposition to fired films it will be used in order to make the evaluation of the bismuth oxide addition as easy as possible. In addition to the firing, all other controllable variables involved in the processing of ink SPC2-YZ will remain as close as possible to those used for ink SPC1-YZ in order to insure a valuable comparison between the inks.

## 4.3 Adhesion Studies

The primary test for evaluating the effectiveness of bismuth oxide as an adhesion promoter will be the Scotch tape adhesion test. As

STANDARD FIRING SEQUENCE #1 PROFILE
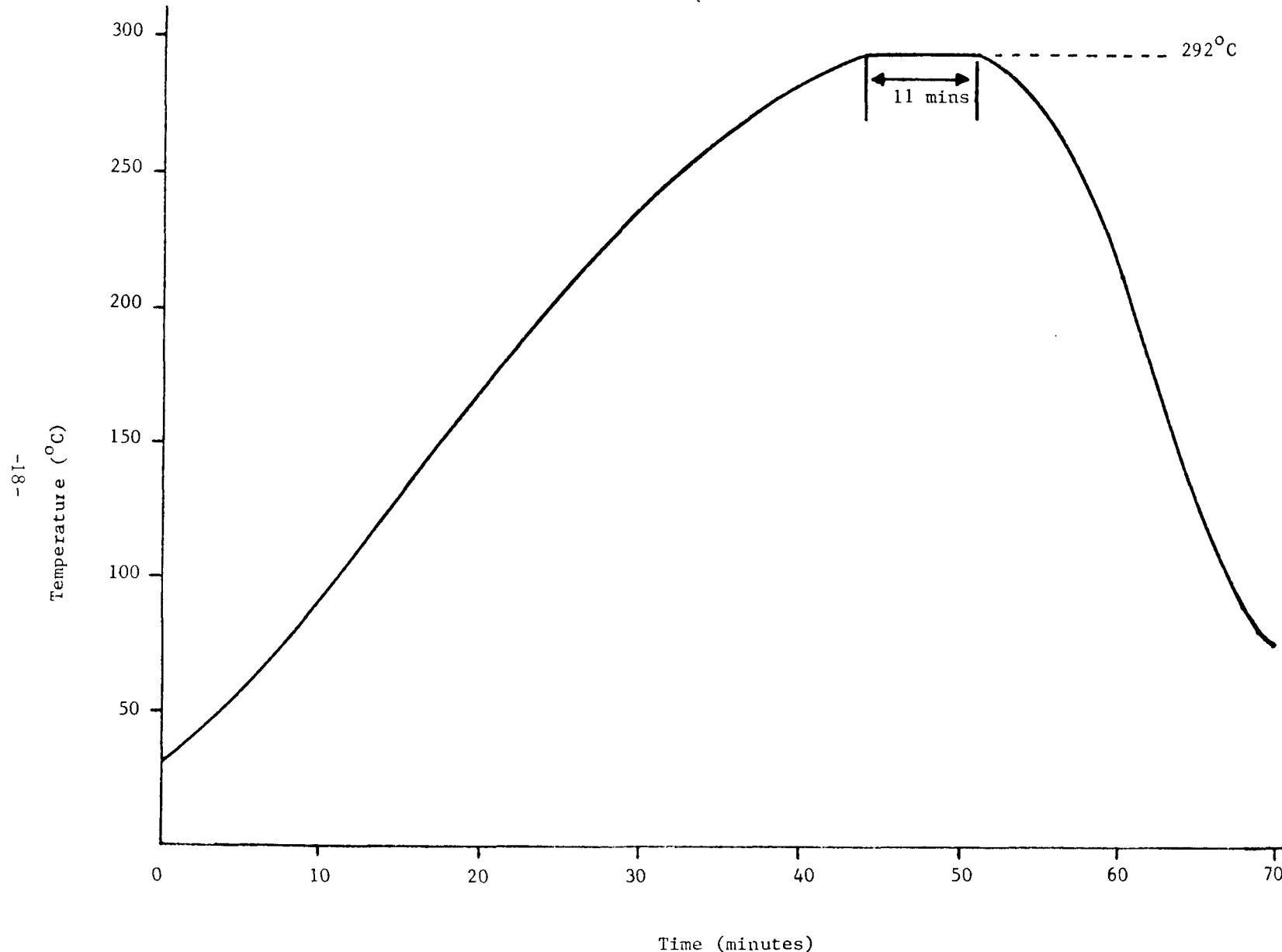
Figure 1.  Profile for Standard Firing Sequence #1.

outlined in previous quarterly reports, this provides a simple and fast qualitative determination of adhesion strength of the fired film to the solar cell. In order to fully evaluate bismuth oxide's effectiveness, long term adhesion studies will have to be conducted. The fired films for these tests will be stored in a dessicator in order to eliminate environmental effects on the metallizations. One or two cells will be removed from the dessicator at periodic intervals in order to monitor the long term adhesion. Previous long term adhesion studies of films printed with SPC1-YZ were not done using a dessicator; so in order to eliminate this variable a set of films will be printed from ink SPC1-YZ and subjected to a long term adhesion study using dessicator storage between tests.

## 4.4 Multi-Layer Film Considerations

Once the presence of bismuth oxide in the fired films was shown to improve long term adhesion, as will be documented in section 5.3, it was necessary to consider multi-layer film formation. This is necessary for two major reasons. The first concerns the MOD thick film technology itself since films produced by this method are usually considerably thinner than conventional thick films. In the case of single layer silver films screen printed through a 325 mesh screen the thickness has been estimated to be between 0.5 and 0.8 microns. Even with pure silver films this thickness is so small that the series resistance is too high. The addition of platinum or bismuth oxide further complicates this problem. Unfortunately, such thin films usually do not plate up very well by common electro-plating methods since the films dissolve in the plat-

ing bath almost instantaneously before the plating operation has a chance to begin. Therefore, MOD screen printed films will often need to be built up to at least several microns before plating can be done. This is best accomplished by printing successive layers directly on top of one another.

The second reason for the necessity of multi-layer films became apparant after the addition of bismuth in the form of bismuth oxide. Although the platinum addition to the silver films to promote solder leach resistance did not seriously degrade the film's electrical resistivity, the presence of bismuth oxide in any significant quantity is considerably more damaging. The relatively large amount of bismuth added (5 w/o) in the first studies was especially bad for film resistivity. In order to overcome this problem additional layers can be added without bismuth 2-ethylhexanoate such that the bismuth oxide will be present only at the substrate/film interface where it is needed to promote adhesion. Theoretically, successive layers should adhere to one another without the need of any type of bonding agent. These upper layers without bismuth oxide will thereby help decrease the overall film resistivity by lowering the relative bismuth oxide content while also giving a higher volume film.

The major consideration in producing multi-layer films is what heat treatment, if any, should be conducted between layers. It is also important to consider whether a heat treatment, once selected, will be needed between all layers or only after every other or every third layer for example. As documented in quarterly report #3, research with multi-layer, especially two layer, silver-platinum films revealed that

either a drying step or a firing step, but not both, was needed between layers. It was also learned that simple successive printings without any heat treatment between layers gave films with poor line definition. It should be noted that in no cases were more than three layer films produced and in fact only a limited number of three layer films were produced due to alignment problems with the screen printer. Nonetheless, these results will be carried over to the current research such that at first only the quicker and more economical batch drying step will be used between successive layers. Since as many as six layer films will be attempted, at least one intermediate firing step may be needed to remove the organic from the lower layers before the last layers are added. Such a step should prevent film cracking due to organic removal.

Regardless of the heat treatment eventually selected for multi-layer films, both initial and long term adhesion as well as adequate line definition will need to be maintained. This latter film quality can be especially difficult to maintain without proper ink rheology. Any significant amount of spreading makes it very difficult to maintain line definition while successively adding layers. The screen printer alignment problems mentioned above, which can also make obtaining acceptable line definition very difficult, have been corrected and should not cause any problems with current research.

## 4.5 Mercury Vapor Leaching Progress

The modifications to the mercury vapor leaching apparatus were completed late in this quarter. These were, a decrease in the length of

the water cooled sample mounting bar and a decrease in the height of the siphon connecting the heated mercury bath and collection pool beneath the sample holder. With these modifications completed, it became possible to remove the films from the solar cells for interface examination.

Initial testing of the apparatus led to the belief that films could be completely removed within one hour of leaching. However, microscopic examination of these samples revealed what was apparently a considerable amount of film still on the solar cell surface. Unless the films are removed to the greatest possible degree (within a reasonable amount of time), interface examination under the SEM will not be very valuable especially if EDAX composition analysis is to be employed. Further testing has shown that at least 3-4 hours will be needed for each sample in addition to the mount curing time of 24 hours prior to testing.

Due to time constraints late in the quarter samples acceptable for interfacial examination have yet to be produced. It is expected that research will proceed in earnest in this area early in the new research quarter.

## 5. RESULTS AND DISCUSSION

### 5.1 Evaluation of Metallization Process for Causes of Adhesion Loss

Although little has been learned or is known about the bonding mechanism of thick film MOD silver conductor films to silicon, the results obtained so far strongly suggest the presence of a weak, process-sensitive bond. There are a considerable number of variables

which can influence film adhesion to a substrate to some degree, and one of them is substrate surface roughness as discussed in Section 3.2. A reclamation process using dilute nitric acid was instituted since no virgin alkali etched cells were left for this study. Films printed with ink SPC1-YZ and fired at the same time on the virgin and reclaimed acid etched cells gave similar adhesion results by the Scotch tape test. These were good to excellent for single layer films and fair for 2 layer films. In fact, the reclaimed cells gave slightly better adhesion results than the virgin cells. The reclamation process did not visibly or microscopically (100X) change the surface of either alkali or acid etched cells. Once the reclamation process was deemed safe in terms of not influencing the film adhesion, a direct comparison was made between film adhesion on reclaimed alkali etched cells and film adhesion on either virgin or reclaimed acid etched cells. The results obtained from this comparison were neutral for the most part in terms of adhesion differences for the two surface roughnesses. In fact, the results were in some respects opposite to what was expected since if there was to be a difference, the rougher alkali etched cells would logically give the better adhesion. In reality, the direct side-by-side comparison showed similar results although for both single and double layer films the smoother acid etched cells gave slightly better adhering films. These results eliminated the difference in surface roughness as a possible cause for the sudden loss of initial adhesion.

Another potential cause for the loss of initial adhesion rests with the ink itself. With the exception of the very first single and double layer films printed with batches 1 and 2 of ink SPC1-YZ all films had

shown excellent initial adhesion. Both of the non excellent cases were also printed on as-received cells which were not HF cleaned prior to printing so the sudden loss of initial adhesion when batch 3 of the ink was first used was quite unexpected. A new batch of SPCl was formulated, and fired films made from it showed excellent single, double and triple layer adhesion both initially and after 4 days. As determined by dried film thickness measurements, these films were similar in average thickness (measured at 10 different points in the pattern) to films made from batch 3 which had given less than satisfactory initial adhesion. These results suggested that there may have been a problem unique to batch 3 of ink SPCl which gave the poor initial adhesion results. However, batch 6 of the ink printed and fired later in the quarter also showed only good initial adhesion. The inability to produce batches of ink which give films with consistently excellent initial adhesion when the exact same formulation procedure is used reinforces the need for a permanent binding agent.

The final area investigated in the search for the adhesion loss cause was the processing of the printed films. There are two main segments to this area, film thickness and firing. Any variations in printed film thicknesses can cause different adhesion results if the variations are large enough, since different optimum processing may be required for films of different thicknesses. Since a given ink is formulated in the same manner each time and since the printing operation is done in the same manner, significant variations in printed film thickness should not occur. Nonetheless, variations in the screen and squeegee due to wear can cause variations. The dried film thicknesses

were monitored in order to detect any significant variations in film thicknesses during or between printings. Thus far, there has been very little, if any, evidence which suggests that variations in film thicknesses are responsible for the loss of initial adhesion.

The second segment to the processing area which could strongly influence resulting adhesion is the firing. The belt furnace profile was re-checked after the adhesion problem was first noticed even though the furnace settings have remained constant since the establishment of standard firing sequence #1. This profile re-check did reveal some differences from the original profile including slightly faster heating and cooling rates and a $10^{o}C$ higher maximum temperature. Whether or not these differences are significant enough to cause the poor adhesion results is unknown. However, the fact that the furnace profile varies at the same settings merits frequent checking of the profile.

## 5.2 Initial Processing Studies with Ink SPC2-YZ

The initial results from processing studies conducted with ink SPC2-YZ have been very promising. The rheology of the ink was very compatible to screen printing, and on-screen stability and long term (at least one month) storage stability were very good. Test no. 3 in Table 5.1 was the first test using ink SPC2-YZ. The single layer films had excellent line definition as rated by the system established for the JPL pattern in quarterly report no. 2. The surface appearance was smooth but the films had a strong grey tint instead of the familiar whitish silver color associated with silver and silver/platinum films. The initial film adhesion was excellent by the Scotch tape test as was the long

Table 5.1  FIRING STUDY RESULTS FOR INKS SPC1-YZ, SPC2-YZ AND COMBINATIONS OF BOTH.

| Test #[a] | Ink # | # of layers | firing sequence | solar cell[b] batch # | line defin. | sheet resist. (mΩ/sq) | initial adhesion |
|---|---|---|---|---|---|---|---|
| 1 | #38 plain Ag ink; Age-1 day; R.H.=58% | 1 | Std. firing sequence #1[c] | 346-193 | A | 39.1[d] | excellent |
| 2 | SPC1-3B Age-14 days R.H.=57.5% | 1 | Std. firing sequence #1 | 346-193 | A | 44.1[d] | good |
| 3 | SPC2-1A[e] Age-16 days R.H.=42% | 1 | Std. firing sequence #1 | 346-199 | A | 173.2[d] | excellent |
| 4 | SPC1-6A[f] Age-1½ hrs. R.H.=40% | 1 | Std. firing sequence #1 | 346-199 | A/B | 51.6 | good |
| 5 | SPC2-1B[g] Age-28 days R.H.=41% | 1 | Std. firing sequence #1 | 346-199 | A | 139.5 | excellent |
| 6 | SPC1-6B[h] Age-3 days R.H.=41% | 2 | Std. firing sequence #1[i] | 346-199 | A | 59.2 | excellent |

(a)  Tests 5-9, 10-11, 12-14 are part of 3 individual multi-layer studies.

(b)  All solar cells were cleaned by HF cleaning procedure prior to painting. (Refer to quarterly report #3 for this procedure).

(c)  See Section 4.2

(d)  For films of similar thickness as determined by fired film thickness measurements.

(e)  Test 3 films used in long term adhesion study.

(f)  Test 4 films used in long term adhesion study.

(g)  Films not used for multi-layers were combined with test 4 films for long term adhesion study.

(h)  Tests 6-9 have bottom layer printed with SPC2-1B (see test #5) and SPC1-6B in layers 2-5.

(i)  Std. firing sequence #1 after final layer only.  A batch drying step of 30 mins. at 65°C is done between previous layers.

Table 5.1 Continued.

| 7 | SPC1-6B<br>Age-3 days<br>R.H.=41% | 3 | Std. firing<br>sequence #1 | 346-199 | B | 47.1 | poor on bus<br>bar[j]<br>good on nar-<br>row lines |
|---|---|---|---|---|---|---|---|
| 8 | SPC1-6B<br>Age-3 days<br>R.H.=41% | 4 | Std. firing<br>sequence #1 | 346-199 | B | 41.6 | poor on bus<br>bar[j]<br>good on nar-<br>row lines |
| 9 | SPC1-6B<br>Age-3 days<br>R.H.=41% | 5 | Std. firing<br>sequence #1 | 346-199 | B | 41.0 | poor[j] |
| 10 | SPC2-2A<br>Age-16 days<br>SPC1-6C<br>Age-19 days<br>R.H.=49% | bottom<br>2<br><br>top | Std. firing[i]<br>sequence #1 | 346-199 | A/B | 38.6 | excellent |
| 11 | SPC1-6C[k]<br>Age-19 days<br>R.H.=49% | 4 | Std. firing[l]<br>sequence #1 | 346-199 | B | 17.8 | poor on bus<br>bar[m]<br>excellent on<br>narrow lines |
| 12 | SPC2-2B<br>Age-18 days<br>R.H.=36% | 1 | Std. firing<br>sequence #1 | 346-199 | B | 79.9 | excellent |
| 13 | SPC1-6D[n]<br>Age-21 days<br>R.H.=36% | 2 | Std. firing<br>sequence #1<br>after each<br>layer | 346-199 | A/B | 29.5 | fair on bus<br>bar, excellent<br>on narrow<br>lines |
| 14 | SPC1-6D[n]<br>Age-21 days<br>R.H.=36% | 3 | Std. firing<br>sequence #1<br>after each<br>layer | 346-199 | B | 19.7 | poor on bus<br>bar[m]<br>*excellent on*<br>narrow lines |
| 15 | same films<br>produced by<br>test #10 | 2 | Refire films<br>using std.<br>firing sequence<br>#1 w/o drying step | 346-199 | A/B | 38.6 | excellent[o] |

(j)  Cracks visible to naked eye on bus bar after firing.

(k)  Bottom layer is printed with SPC2-2A.

(l)  Std. firing sequence #1 is done after layers 2 and 4.   A 30 min./65°C batch dry is done after layers 1 and 3.

(m)  Cracks revealed in bus bar under lower magnification after firing.

(n)  Ink SPC2-2B used for bottom layer.

(o)  Checked immediately before and after refiring.

term adhesion as will be discussed in the next section of this report. The most dramatic result for these new films besides the greatly improved long term adhesion is the film resistivity. As can be seen by comparing tests 1, 2 and 3 in Table 4.1, the presence of bismuth oxide in the film had a drastic negative effect on the sheet resistance. The effect of a 4 w/o platinum addition to the ink was not too significant since platinum is a very good conductor with a resistivity of 10.6 $\mu\Omega$-cm compared to silver's 1.59 $\mu\Omega$-cm. However, the addition of 5 w/o Bi in the form of bismuth oxide caused an increase in sheet resistance by more than a factor of 4. Tests 5 and 12 also show very large values of sheet resistance for single layer films containing bismuth oxide, although these values were not as high as in test 3. This is because slightly higher quality, thicker films were produced in tests 5 and 12 after a new screen was installed on the screen printer. Nevertheless, the presence of bismuth oxide is damaging to the film's electrical properties and will certainly need to be minimized while not sacrificing its ability to impart adhesion for an indefinite amount of time.

Some purely qualitative notes can be made about the films made from ink SPC2-YZ. The adhesion was often rated excellent for single layer silver/platinum films made from ink SPC1-YZ, but the films made from this new ink were clearly better adhering in terms of the difficulty encountered in pulling up the Scotch tape during the adhesion test. Additionally, these latest films containing bismuth oxide are apparently much harder than silver or silver/platinum films since they no longer easily scratch when the resistance meter probes are applied. A final note on the film appearance deals with the possibility of the films tar-

nishing over time. When an adhesion test was performed on the film made from SPC2-1B after 65 days in a dessicator, a yellowish residue was removed by the tape from the film surface although the film itself remained strongly intact. Although the exact nature of this residue has not been investigated as of yet, it is something to be aware of in the future.

## 5.3  Long Term Adhesion Studies

All the films produced in test 3 (Table 5.1) and those from test 5 not used for multi-layer studies were stored in a dessicator. Either one or two films was removed for an adhesion test after 1, 2, 3, 5, 8, 10, 15, 21, 27, 35 and 65 days. The results of these tests need not be tabulated since the adhesion remained excellent (100%) throughout the entire test (the test was terminated when the films ran out). Previous long term adhesion tests conducted during the third quarter on silver/platinum films from ink SPC1-YZ were not done using a dessicator. In order to eliminate this variable, a set of films were printed (initial properties are under test 4 in Table 5.1) using ink SPC1-6A and stored in a dessicator. This time one or two films were adhesion tested after 1, 3, 4, 5, 8, 12, 18 and 26 days. The adhesion remained good (85 - 95%) throughout this study (the 12 day film even showed an improvement to excellent adhesion) which may suggest that humidity or other atmospheric impurities may accelerate adhesion degradation. The storage in the relatively constant environment of the dessicator seems to considerably slow or prevent degradation although this phenomena will require further investigation. However, this discovery does not in any way

diminish the necessity of bismuth oxide in the films since consistent excellent initial adhesion cannot be obtained without it as evidenced by batches 3 and 6 of ink SPC1-YZ.

## 5.4  Multi-Layer Films

JPL has suggested a 10 µm goal for the thickness of films produced with MOD inks by screen printing, which will require a minimum of 6-7 layers since single layer MOD films probably have a maximum limitation on fired thickness of 1.0 to 1.5 µm. In addition to this relatively large number of layers required, the other major consideration is the choice of composition for each of the layers. Theoretically, only the bottom layer will need to contain bismuth oxide for adhesion to the sub-strate since intermediate layers should adhere to each other without difficulty. Also, only the top one or two layers should require the platinum addition for solder leach resistance. This former composi-tional requirement is especially critical due to the previously docu-mented effects of bismuth oxide on film resistivity (the platinum, although its presence should be minimized, has much less of a negative effect on resistivity). Due to the availability of stable inks SPC1-YZ and SPC2-YZ, the first research conducted used bismuth oxide in the bot-tom layer only with silver and platinum in all layers.

Four sets of tests were conducted during this quarter to produce multi-layer films, and as expected several problems were encountered. The first set, tests 5-9 in Table 5.1, used ink SPC2-YZ in the bottom layer and ink SPC1-YZ in all additional layers with either a 30 min/65$^{\circ}$C batch drying step only between layers or standard firing sequence #1

after each new layer was added. As can be seen in Table 5.1, the sheet resistance decreased by more than 1/2 and 2/3 for the second and third layers respectively as would be expected, but further decreases with the addition of 4 and 5 layers were less than expected. More importantly, the loss of adhesion after a third layer was added and the simultaneous presence of cracks (easily visible with the naked eye) in the connecting bus bar of the fired films are of greater concern. The logical explanation for this is that the cracks are caused by the decomposition products from the lower layers which must force their way up through the film resulting in severe film cracking. These cracks in turn cause both the poor adhesion results and the less than expected decrease in film sheet resistance. The cracking and adhesion problems were limited to the wider and often thicker connecting bar until the fifth layer was added, at which point the adhesion was poor for the entire metallization. On a more positive note, the line definition was acceptable for all the films including the 5 layer ones which suggests that the ink viscosities are suitable for multi-layer films such that very limited spreading or bleed-out occurs during the post-printing or heat treatment stages.

In order to offset the problems apparently caused by decomposition product removal, the next studies involved firing after every other and then after every layer in order to periodically remove the organics. The results for these tests, shown in Table 5.1 under tests 10-11 and 12-14 respectively, did not lead to a correction of the problem although the sheet resistance values were greatly improved and the line definitions continued to be acceptable. In fact, as noted in test 13, a

degradation in adhesion occurred for a two layer film although no cracks were visible even under 100X magnification. It should also be noted in test 11 that although no cracks were found in the 4 layer films on which adhesion tests were done, there were several samples which did have severe bus bar cracking. The only possible explanation from a purely heat treatment standpoint is that the refiring of a previously fired layer causes a breakdown in adhesion. Test 15 was used to evaluate this possibility, and although only a few films were tested the results did not provide the desired explanation. As can be seen, the adhesion remained excellent and the electrical sheet resistance did not change after refiring two layer films from test 10 which had been stored in a dessicator for one week.

These multi-layer film results have left the research in this area at a brief standstill. Two possible solutions which will be evaluated in the next quarter are a change in ink chemistry and the implementation of a new firing profile using a much slower heating rate. The change in chemistry would be to keep the composition constant for all layers with a reduced bismuth oxide content throughout. The reason for this is the possible existance of a chemical gradient in the metallization caused by the absence of bismuth oxide in all but the bottom layer. In theory, it is possible that this chemical gradient can act as a driving force which may influence the film adhesion or cracking occurrance to some degree. The use of a slower firing rate may be helpful in the organic removal process during decomposition by allowing a slower, less disruption removal of the decomposition products. The fact that acceptable five layer line definition has been obtained as well as significant decreases in

sheet resistance with increasing thickness make the search a successful multi-layer film processing sequence worthwhile.


## 6. FUTURE PLANS


Research during the next several months through the remainder of the contract will be concentrated in four main areas; ink composition optimization, processing, broadening the adhesion model and environmental testing. In order to optimize the ink composition, the platinum addition will be temporarily omitted while the bismuth oxide addition is optimized, and then reinstated and optimized. Processing studies will concentrate in the near future on slower firing in an attempt to eliminate film cracking in multi-layer films. To fully develop an adhesion model, considerable effort will be applied to the mercury vapor leaching area as well as to both electron and conventional microscopy studies. Finally, after the ink composition is at least somewhat better optimized, environmental testing of the metallizations can begin with emphasis on studying environmental effects on adhesion. This research will be done by making use of a environmental and thermal cycling furnace available in Turner Laboratory.


## 7. SCHEDULE


The list of tasks and the updated program plan are attached.

| Task No. | Description |
|---|---|
| 1 | Ink Development |
| 2 | Processing Studies |
| 3 | Fabricating Cells |
| 4 | Characterizing the Cells |
| 5 | Environmental and Operational Testing on Fabricated Units |
| 6 | Specifications |
| 7 | Adhesion Model |
| 8 | Data for Economic Evaluation |
| 9 | Personnel for Meetings |
| 10a | Monthly Technical Reports |
| 10b | Quarterly Technical Reports |
| 10c | Final Technical Report |
| 10d | Monthly Financial Management Reports |

TASK
NO.

-35-

DATE