

NASA CR 72382
Project 303350

CdS SOLAR CELL DEVELOPMENT

INTERIM TECHNICAL REPORT

February 29, 1968

Contract No. NAS 3-9434

National Aeronautics and Space Administration
Lewis Research Center

By: F. A. Shirland
W. K. Bower
J. B. Green

Clevite Corporation
Electronic Research Division
Cleveland, Ohio 44108

TABLE OF CONTENTS

	Page
LIST OF ILLUSTRATIONS	iii
LIST OF TABLES	iv
I INTRODUCTION	1
II CELL FABRICATION	2
A. Standard Cell Design	2
B. Fabrication Process	2
1. Substrate Preparation	4
2. CdS Evaporation	4
3. Barrier Formation	4
4. Grid Attachment	5
5. Cover Plastic Attachment	5
6. Final Cell Preparation	6
C. Quality Assurance	6
D. Yields	6
E. Cell Outputs	9
III STABILITY CHARACTERIZATION	12
A. Dry Shelf Storage	12
B. Moisture Resistance	15
C. High Temperature Storage	19
1. Storage at 100°C, 10 ⁻⁴ Torr	19
2. Storage at 150°C, 10 ⁻⁴ Torr	19
D. Thermal Cycling	26
1. Boeing Test - NASA, Lewis Contract - April 1967 Production Cells	27
2. Boeing Test - Lincoln Lab Contract - July 1967 Production Cells	27
3. NASA Lewis Laboratory Test - October 1967 Cells	32
4. M.I.T. Lincoln Laboratory Test - Oct. & Dec. 1967 Cells	37
5. Other Tests	37
6. Analysis of Degraded Cells	40
(a) Changes in Electrical Output	40
(b) Physical Changes	44
(c) Interpretation of Results	46

	Page
IV CELL DESIGN IMPROVEMENTS	47
A. Semiconductor - Substrate Interlayer	47
1. Chromium	48
2. Aluminum	48
B. Copper Substrate	49
C. Evaporated Grid Contact	49
D. Alternate Grid Designs	52
E. Alternate Cover Plastics	52
V FABRICATION PROCESS IMPROVEMENT	53
A. Substrate Preparation Process	53
B. CdS Film Evaporation	55
C. Grid Contact	56
D. Lamination Process	57
1. The Epoxy Cement	57
2. The Cell Cracking Problem	57
3. Lower Lamination Pressure	58
E. Cell Testing	58
1. I-V Characteristic Test Equipment	58
2. Calibration	59
3. Spectral Response Measurements	59
REFERENCES	62
APPENDIX I QUALITY ASSURANCE PROGRAM	

LIST OF ILLUSTRATIONS

FIGURE		Page
1	Construction and Dimensions of Clevite Plastic Substrate CdS Thin Film Solar Cell	3
2	Fabrication Steps and Inspection Points	7
3	Standard Process Cell Efficiencies - Mylar Cells	10
4	Standard Process Cell Efficiencies - Kapton Cells	11
5	"Hysteresis" Effect Observed on Boeing Thermal Cycling Test	30
6	Erratic I-V Curve Traces Obtained on Boeing Thermal Cycling Test	31
7	Erratic Degradation of Maximum Power on Thermal Cycling Test	41
8	Effect of Thermal Cycling on I-V Characteristic Curve - April 1967 Cell	42
9	Effect of Thermal Cycling on I-V Characteristic Curve - October 1968 Cell	43
10	Lateral Cracks and Delaminations Observed After Thermal Cycling	45
11	Spectral Response of Kapton Covered Cell	61

LIST OF TABLES

Table		Page
I	Yields from Standard Cell Fabrication Line	8
II	Dry Shelf Storage - Long Term Test Data	13
III	Dry Shelf Storage - Shorter Term Test Data	14
IV	Wet Shelf Storage - Long Term Test - Original Data	16
V	Wet Shelf Storage - Long Term Test - Corrected Data	17
VI	Wet Shelf Storage - Shorter Term Test Data	18
VII	100°C Vacuum Storage - Longer Term Data	20
VIII	100°C Vacuum Storage - Corrected Data - 4 Best Cells	21
IX	100°C Vacuum Storage - More Recent Cells	22
X	150°C Vacuum Storage	24
XI	Effect of 150°C Vacuum Storage on Efficiency, Capacitance and Dark Diode Characteristic	25
XII	Clevite Test Data on Cells Used for Boeing Thermal Cycling of April 1967 Production	28
XIII	Boeing Thermal Cycling Data on April 1967 Cells	29
XIV	Clevite Test Data on Cells Used for Boeing Thermal Cycling of July 1967 Production	33
XV	Boeing Thermal Cycling Data on July 1967 Cells	34
XVI	Clevite Test Data on Cells Used for Lewis Lab Thermal Cycling of October 1967 Production	35
XVII	Lewis Lab Thermal Cycling Data on October 1967 Cells	36
XVIII	Clevite Test Data on Cells Used for Lincoln Lab Thermal Cycling of Oct. - Dec. 1967 Production	38
XIX	Lincoln Lab Thermal Cycling Data on Oct. -Dec. 1967 Cells	39
XX	Performance Data of Aluminum Interlayer Cells	50
XXI	Performance of Cells with Evaporated Gold Grids and Overlaid Standard Cemented Metal Mesh Grids	51

I. INTRODUCTION

This report summarizes a year's development of the plastic substrate CdS thin film solar cell under Contract NAS 3-9434. This is the continuation of a series of earlier NASA contracts (1, 2, 3) on the CdS thin film solar cell at the Clevite Research Center.

The present program's major objectives were: cell design improvement (including the conductive plastic substrate, increasing area utilization, and larger cells); higher cell efficiencies; characterizing the CdS thin film cell (particularly its stability); and operating a cell fabrication line to make 100 cells per month.

Part way into this program work on the cell design improvements was reduced and increased efforts were placed on characterizing cell stability and on achieving better control over the process of fabricating the cells. The processes for attaching the grid and for cementing the cover plastic were singled out for additional development, but all of the fabrication processes as well as the raw materials and component parts used in the cell were to receive better inspection and quality assurance procedures in an effort to improve cell reproducibility.

Still further into the Contract it became evident that the cells being fabricated were not remaining stable when placed in a vacuum chamber and temperature cycled to simulate the conditions expected on a space vehicle in a low altitude earth orbit. The reasons for the loss of cell output on these tests were not evident, though an intrinsic change in the semiconductor junction did not seem to be involved. A major shift in emphasis was made therefore toward determining the causes for cell failures during vacuum thermal cycling.

During this reporting period additional tooling and processing facilities were provided and proved-in, as part of a separate Company funded program, which increased cell fabrication capacity to the level of 100 cells per 8-hour day. This was carried out successfully retaining essentially the same cell design and fabrication process.

Many individuals have contributed to the progress reported here. Project direction has been provided by F. A. Shirland. J. R. Hietanen was the principal investigator for the earlier part of the contract period, with F. A. Shirland filling this function during the last few months. The following Clevite personnel also participated in these studies: W. K. Bower, W. F. Dunn, J. B. Green, R. J. Kinley, D. L. Lehmann, H. E. Nastelin, L. R. Shiozawa, R. D. Simonton, L. S. Sliker and J. A. Smith.

L. R. Scudder of the Power Systems Division, Lewis Research Center, NASA, acted as Contract Monitor under the direction of A. F. Forestieri. A. Spakowski of the Chemistry and Energy Conversion Division, Lewis Research Center, NASA, carried out some of the temperature cycling tests and other evaluations reported here. Many other personnel of the Lewis Research Center also were involved in evaluating and testing the cells prepared on this contract and their work is gratefully acknowledged.

In addition, A. Stanley and other personnel of M.I.T. Lincoln Laboratory ran some thermal cycling tests and other analyses of the cell which contributed substantially to a better understanding of the weaknesses in the present cell design.

II. CELL FABRICATION

A. Standard Cell Design

The design of the CdS thin film solar cell has not changed substantially over the period of this study. The standard cell is still nominally 3" x 3" in size. The construction and detailed dimensions are shown in Figure 1.

The active cell area has remained fixed at 74 mm x 74 mm for a total of 54.75 cm². All cell efficiency data presented in this report are based on this area unless otherwise specifically stated. The size of the negative lead tab and the amount of overlap of the cover plastic have varied somewhat during this period, but the tolerances on these have gradually been tightened and in the last few months of the period have more nearly approximated those shown in Figure 1.

The substrate consists of Kapton plastic film, 1 mil thick, which is given a 0.25 to 0.30 mil thick conductive coating on one surface. An extension of this conductive substrate forms the negative lead tab. The CdS semiconductor is a polycrystalline film approx. 1 mil thick. There is a very thin zinc interlayer between the CdS film and the conductive substrate to ensure an ohmic contact between the substrate and the CdS.

The barrier layer is Cu₂S formed on the upper surface of the CdS film. A metal mesh collector grid is attached to the barrier with a conductive epoxy cement. An extension of this grid forms the positive electrode tab of the cell. A narrow insulating strip of Kapton plastic is placed under the grid where it crosses the edge of the cell to prevent shorting to the conductive substrate.

The package is completed by attaching a 1 mil thick cover of either Mylar or Kapton plastic, using a clear epoxy resin as cement. The grid is copper which has been gold plated, and the negative electrode tab is given a copper undercoating and then a flash gold plating for tarnish resistance and solderability. The entire cell package is about 4 mils thick, except at the lead tabs.

The collector grid is 0.45 mils thick and has a rectangular grid pattern with 60 "wires" per inch in one direction and 10 "wires" per inch in the other. The "wires" are nominally 0.001" wide, but taper to 0.00125" at the tab end from 0.00075" at the far end. There is an 0.014" wide border around the edges of the grid to give it additional physical integrity which is needed during handling and layup. The calculated light transmission of the grid design is 91% but actual light transmission of the grids that have been supplied have generally run about 84 to 85%.

Two holes in the tab of the collector grid are intended as locating holes to facilitate layup and handling. In addition, they serve to ensure that the grids are assembled right side up since they are tapered in cross section as a result of the etching process used to fabricate them.

B. Fabrication Process

The process for making the plastic substrate CdS thin film solar cell is relatively straightforward and consists of about a half-a-dozen major steps. These are: substrate preparation, CdS film deposition, Cu₂S barrier formation, gridding, laminating, and cell finishing.

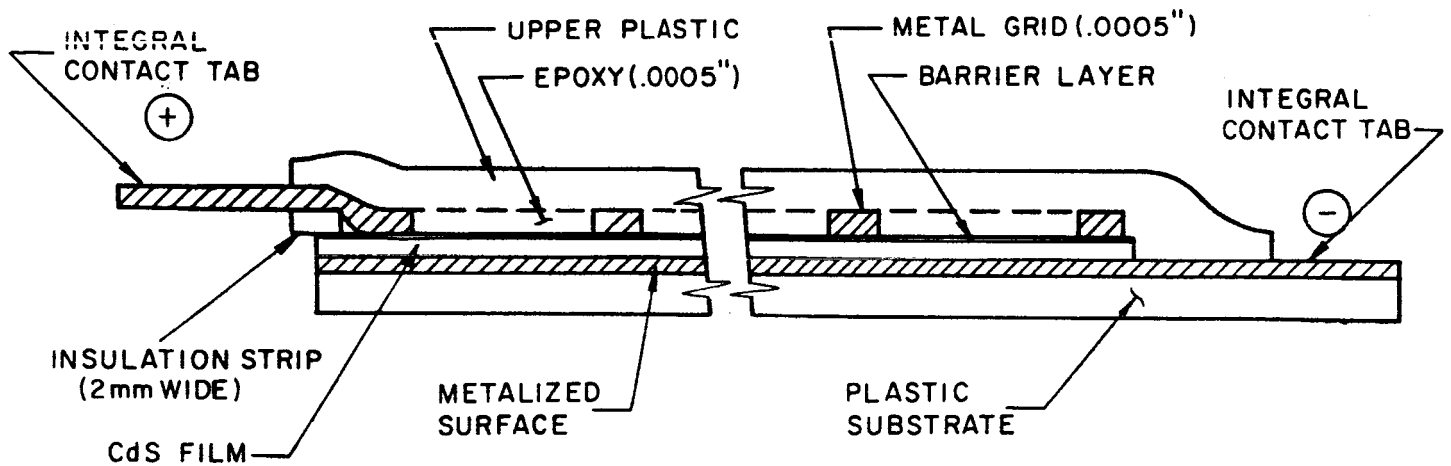
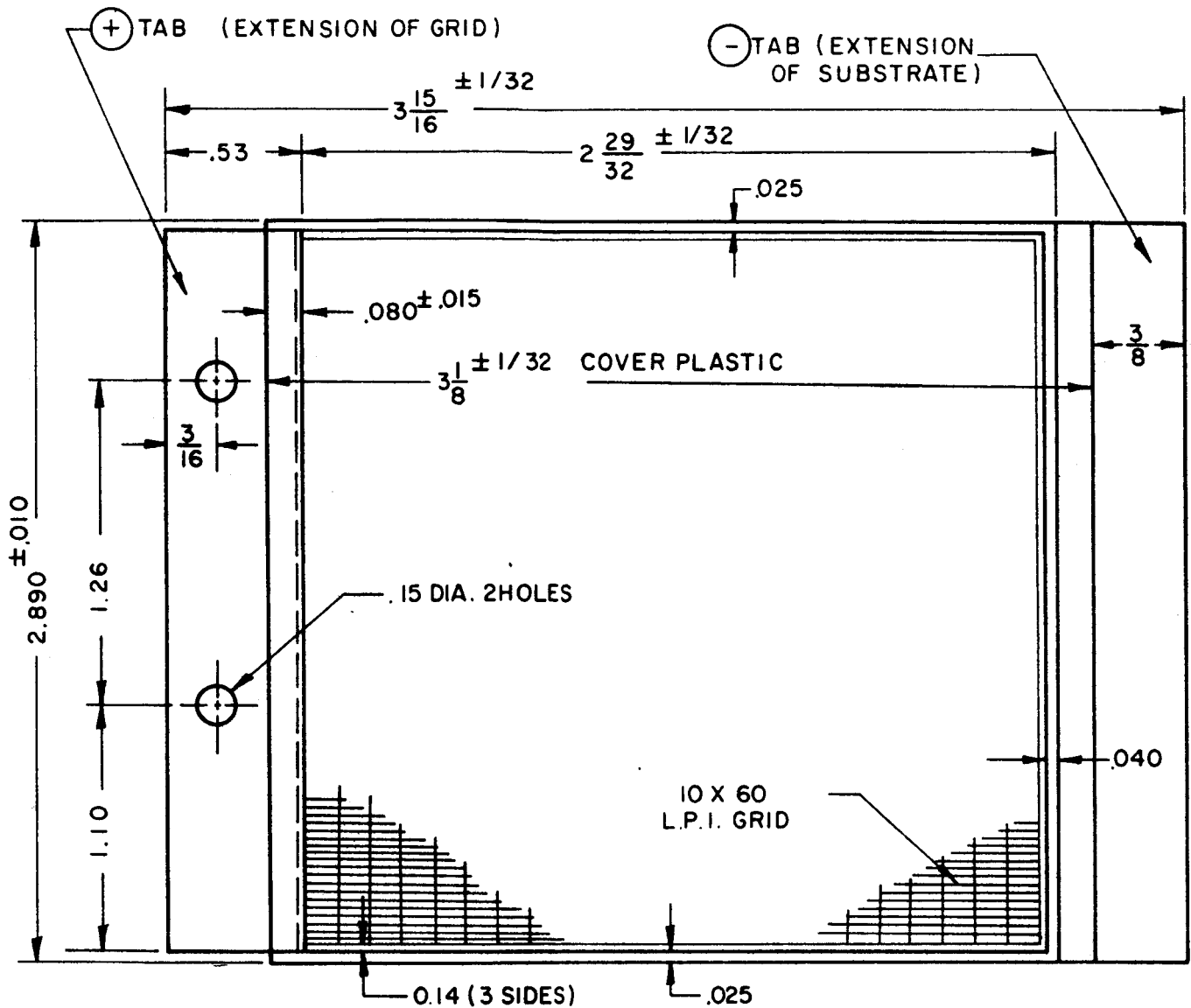


FIG. 1: CONSTRUCTION AND DIMENSIONS OF CLEVITE PLASTIC SUBSTRATE CdS THIN FILM SOLAR CELL.

These processes have evolved over many years. In general, it is the accumulated experience with the conditions and parameters of most of the process steps that enables the fabrication to be carried out successfully, rather than an understanding of what is actually occurring during the operations.

1. Substrate Preparation

A 1 mil thick plastic Kapton film is first cleaned by scrubbing with DMF solvent and then sprayed on one surface with a 1 part silver to 2 parts Pyre-ML by weight solution to a thickness of 0.25 to 0.30 mils. The sprayed substrate is then dried in an oven at 150°C to remove all traces of the DMF solvent and then cured in another oven at 250°C for 30 minutes. Its electrical sheet resistance is measured and held below .01 ohm/sq.

The substrate is then burnished with a Scotch Brite finishing pad mounted on a Rockwell finishing sander to produce a bright, uniformly smooth-textured surface. This operation has been found necessary in order to expose the silver pigment so that suitable electrical contact can be made to it.

The burnished silver Pyre-ML coated plastic substrate is then given a zinc coating by electroplating. The zinc is needed in order to secure good ohmic contact between the silver Pyre-ML and the subsequently deposited CdS film. The uniformity of the zinc electroplating appears to be important in securing a uniform structure CdS film, and the zinc plating must be fresh and free from extraneous contamination in order to secure an adherent CdS deposition.

2. CdS Evaporation

A commercial grade of CdS powder is presintered in vacuum to 850°C and then in argon to 1200°C to remove high vapor impurities and to densify the material. It is then crushed in a mortar and pestle to pass through a 42 mesh screen.

This material is then charged into quartz crucibles in a vacuum evaporator. Vacuum evaporation is carried out at a pressure of 10^{-5} Torr with the substrate held at 220°C. Evaporation is carried out at a rate on the order of 100 to 200A per second. A five minute glow discharge is used during the pump down to assist in cleaning the substrate and special precautions must be taken during the evaporation to prevent spattering of the substrate with ejected CdS particles from the sources.

The resultant CdS films are approximately 20 to 25 microns thick and are n-type semiconducting with carrier concentrations in the range of 10^{17} to 10^{18} per cm^3 resulting from a stoichiometric excess of cadmium. The cadmium sulfide is oriented with the C axis generally perpendicular to the substrate and has an average grain size of approximately a few microns. The conditions of vacuum evaporation do not appear to be very critical and generally satisfactory results have been obtained over a wide range of operating conditions.

3. Barrier Formation

The barrier layer is formed by dipping the CdS film into a hot water solution of CuCl for just a few seconds. The details of this process are largely proprietary, but in general the process consists of Cu^+ ions replacing Cd^{++} ions at the surface of the CdS to form a thin layer of copper deficient Cu_2S . Recent

measurements by L. R. Shiozawa⁽⁴⁾ indicate that this layer is only a few thousand angstroms in thickness and that it appears to take the lattice spacing of the CdS host crystal.

The formation of the Cu_2S layer is followed by a water rinse and an oven drying at 250°C for 2 minutes. From measurements of cells that were heated in argon atmospheres instead of in ordinary air atmospheres, it appears that oxygen plays an important role in securing high efficiency cells, though it is believed that the oven treatment also is required to remove water from the barrier layer.

4. Grid Attachment

The grids are formed by photochemically etching from rolled copper stock by an outside vendor and are then given a flash coating of gold. The purpose of the gold plating is to protect the barrier from contact with any bare copper. It has been found that copper in contact with the barrier has a temporarily degrading effect on cell output in the presence of heat.

A commercial gold filled epoxy resin is then rolled out to a thin layer on a sheet of Teflon plastic. The grid is then laid on this layer of epoxy cement and pressed in so that the gold epoxy transfers to the grid when the grid is removed. This process is highly dependent on the skill of the operator but the techniques are not difficult to acquire and a simple inspection operation following this step ensures that complete coverage of the grids is secured.

The gold filled epoxy coated grid is then placed in position on the barrier surface of the CdS film, and then placed between two sheets of Teflon film. This package is then placed in a special die, covered with aluminum foil and the residual atmosphere exhausted from the package. Positive pressure of 100 psi of nitrogen is applied to the top of the aluminum foil diaphragm. The whole die is heated to a temperature of 196°C and held for 20 minutes. The pressure is maintained on the diaphragm throughout the cycle.

After completion of the gridding cycle the epoxy cement is only set, not fully cured. The cure is completed by soaking the cells in a vacuum oven overnight (18 hours minimum) at a temperature of 135°C .

It is important that the gold epoxy cement be fresh and well mixed, and free from moisture pickup. It is, of course, important that the grids be clean of grease contamination since a poor bond may otherwise result.

5. Cover Plastic Attachment

The cover plastic is a 1 mil thick film of either Mylar or Kapton. It is prepared by spraying with 0.5 mil thick clear epoxy cement which dries to a tack-free consistency thereby permitting the plastic to be handled and stored without difficulty. The cover plastic is applied to the gridded cell and placed in the same die in which the gridding was accomplished. A similar curing cycle is used for the cover plastic except that the cell is held at temperature for 10 minutes instead of 20 minutes. The cure is completed with a similar overnight soaking in the vacuum oven at 135°C .

6. Final Cell Preparation

The final steps in the cell preparation include cleaning and numbering the cells, giving the negative electrode tab a copper electroplating followed by a flash gold electroplating and then trimming the edges to size. The plating of the negative electrode tab is for solderability and tarnish resistance.

Following the clean up operation the cells are inspected for visual defects and then tested electrically for voltage, current and maximum power under standardized test conditions.

The CdS thin film solar cell fabrication processes have been described in much greater detail in the Final Report of the previous contract⁽³⁾. In this period a number of variations to the standard processing conditions have been evaluated and these will be discussed in other sections of this report.

C. Quality Assurance

Early in this contract period it became evident that there was a wide variation in the quality of the cells produced. This variation was obviously the result of wide variations in the raw material and component parts of the cell as well as in the conditions and parameters of the fabrication process itself. Therefore, the preliminary steps for a quality assurance program were made in an attempt to eliminate the wide causes of variation and to bring the entire process under some semblance of control. A full-time inspector was added to the fabrication line and a series of studies were carried out to define acceptable quality levels for the raw materials and component parts of the cell and for the fabrication process itself. Figure 2 illustrates the various steps in the production where inspections were set up. The detailed quality assurance and Pilot Line operator inspections that were evolved are tabulated in Appendix I.

D. Yields

Operation of the standard process cell fabrication line was beset by the usual types of difficulties inherent in making a new product in the laboratory. The cell design, and the basic fabrication process remained virtually unchanged over the period of this report. However, there were major changes in the tooling and equipment used.

A new larger vacuum evaporator that produced 27 standard 3" x 3" CdS films at a time was substituted for the earlier evaporator that produced only 6 such films. This also entailed a change from positioning 6 films on a single sheet of metallized plastic substrate to 9 films on a sheet; and the handling of 9 films on a single sheet through barrier formation from the earlier method of processing them one at a time. The prove-in of the new equipment and tooling took much longer than expected and as a result, the yields were very low for quite a few months.

Table I summarizes the yields from the standard process line for each month of this contract period. The figures are for standard process 3" x 3" cells made on the NASA contract only. Other sizes of cells, experimental cells and cells made for other accounts are not included in Table I.

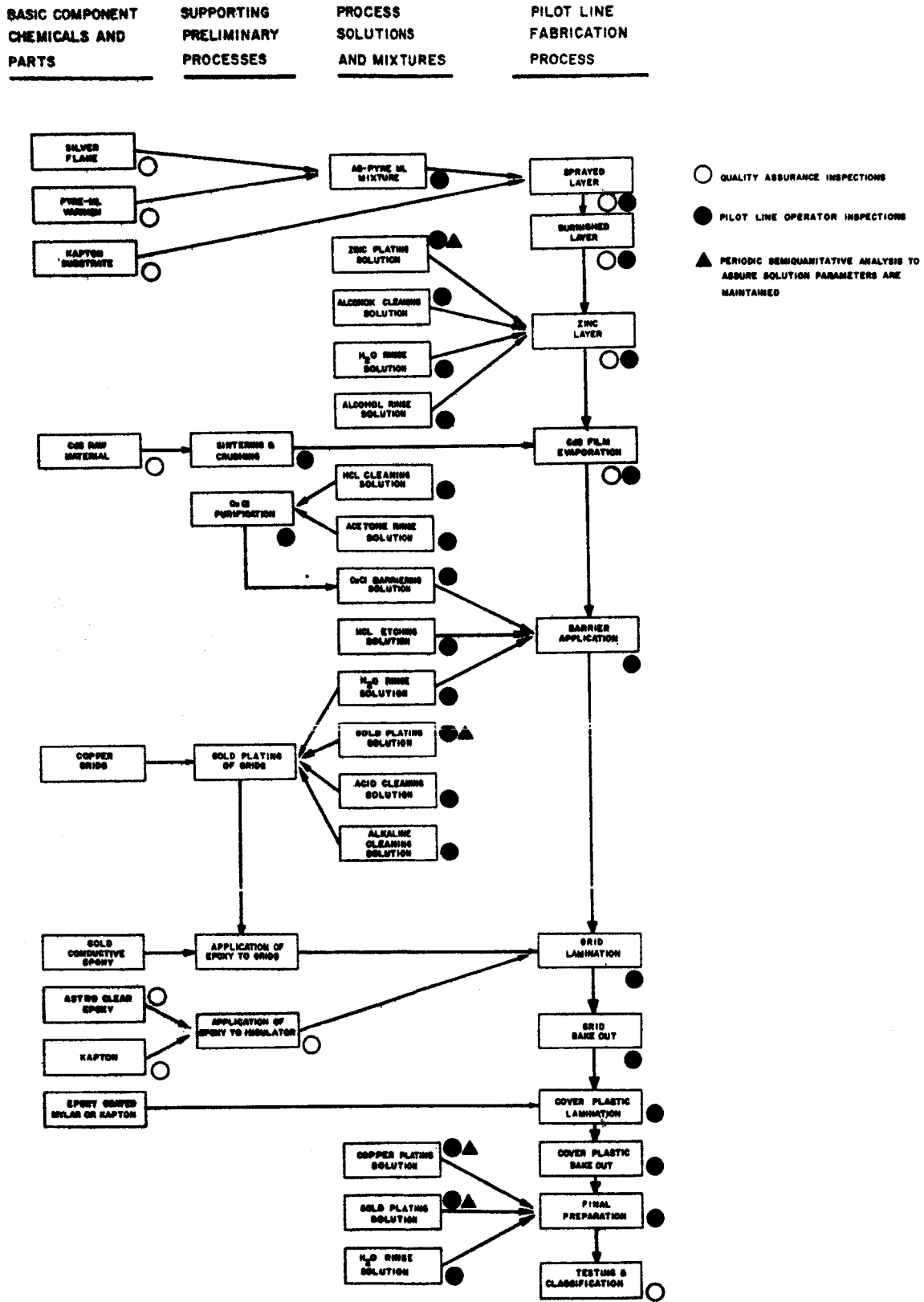


FIGURE 2 FABRICATION STEPS AND INSPECTION POINTS

TABLE I
YIELDS FROM STANDARD CELL FABRICATION LINE

<u>Month</u>	<u>CdS Film Evap.</u>		<u>Barriers</u>		<u>Grid & Laminate</u>		<u>Final Testing</u>	
	<u>Total</u>	<u>Rejects</u>	<u>Total</u>	<u>Rejects</u>	<u>Total</u>	<u>Rejects</u>	<u>Total</u>	<u>Rejects</u>
1	164	3	161	22	139	1	138	37
2	195	12	183	7	176	5	171	70
3	271	16	255	18	237	15	222	122
4	267	42	225	44	181	4	177	77
5	366	93	273	27	246	7	239	139
6	412	60	352	13	339	14	325	225
7	313	64	249	53	196	8	188	108
8	240	1	239	27	212	21	191	91
9	178	0	178	36	142	6	136	36
10	144	0	144	14	130	0	130	30
11	302	14	288	85	203	0	203	38
12	248	9	239	65	174	3	171	33
Total	3100	314	2786	411	2375	84	2291	1006

A total of 3100 CdS films 3" x 3" in nominal size were started through vacuum evaporation and these gave 1285 acceptable quality cells for an overall yield of 41%. There were 314 films rejected after evaporation, and another 411 after barrier formation. The vast majority of these rejects were due to pinholes in the CdS films.

There were only 84 cells rejected during the gridding and laminating operations. Most of these were because of voids in the epoxy cement used to attach the cover plastic, though a few were also due to equipment failures. A total of 1006 cells were rejected at final testing. Low output cells, shorted cells and cells with various dimensional shortcomings, tears or similar visual flaws accounted for most of these. It is difficult to assign definite causes for the low output cells in many cases, but it is believed that the vast majority of the cells scrapped at final testing were directly or indirectly the result of flaws - usually pinholes - in the CdS films. During the latter 4 months of the period, more rigorous inspections of the CdS films were instituted (as part of the quality assurance program) both before and after the barrier formation step. This resulted in fewer rejects in final testing and focused attention to the causes of pinholes so that corrective action could be taken. As a result, in the last 4 months the overall yield increased to nearly 60%.

Even so, pinholes in the CdS films probably remain as the major cause of rejects in this process. Pinholes may result from foreign material in the CdS, from nonhomogeneities at the surface of the substrate or from CdS powder particles spattering onto the substrate from the evaporation sources and subsequently dropping off leaving a pinhole. The pinholes may cause low output or shorted cells from either the short circuiting of the grid to the substrate by way of the conductive epoxy cement, or by precipitation of elemental copper during barrier formation due to the zinc showing through the pinhole.

E. Cell Outputs

Over the period of the present contract very little effort was placed on trying to improve the average efficiency level of the standard production cells. Most of the effort was placed on trying to make the cell reproducibly, to characterize the stability of the cell, and to determine the causes of instability. Hence, only a slight improvement in the cell efficiencies was accomplished over the year and this is believed to have been the result of improved quality assurance measures which were successful in eliminating many of the factors causing low efficiencies.

Figure 3 is a histogram giving the distribution of efficiencies experienced on standard production 3" x 3" Mylar covered cells fabricated during the year. These cells were tested at 25°C in equivalent AM1 sunlight.

Figure 4 presents similar data on the standard cells with Kapton cover plastic. These cells were also tested in equivalent AM1 at 25°C.

A total of 1285 3" x 3" cells were fabricated under standardized conditions during this period. A careful examination of the data suggests that the distribution of efficiencies is still far from what would be expected from a product under control. When the present process is brought under better control, it would probably yield efficiencies averaging about 5.8% for Mylar cover plastic cells in AM1 sunlight at 25°C, and most of the cells would be between about 5.5% and 6.1%.

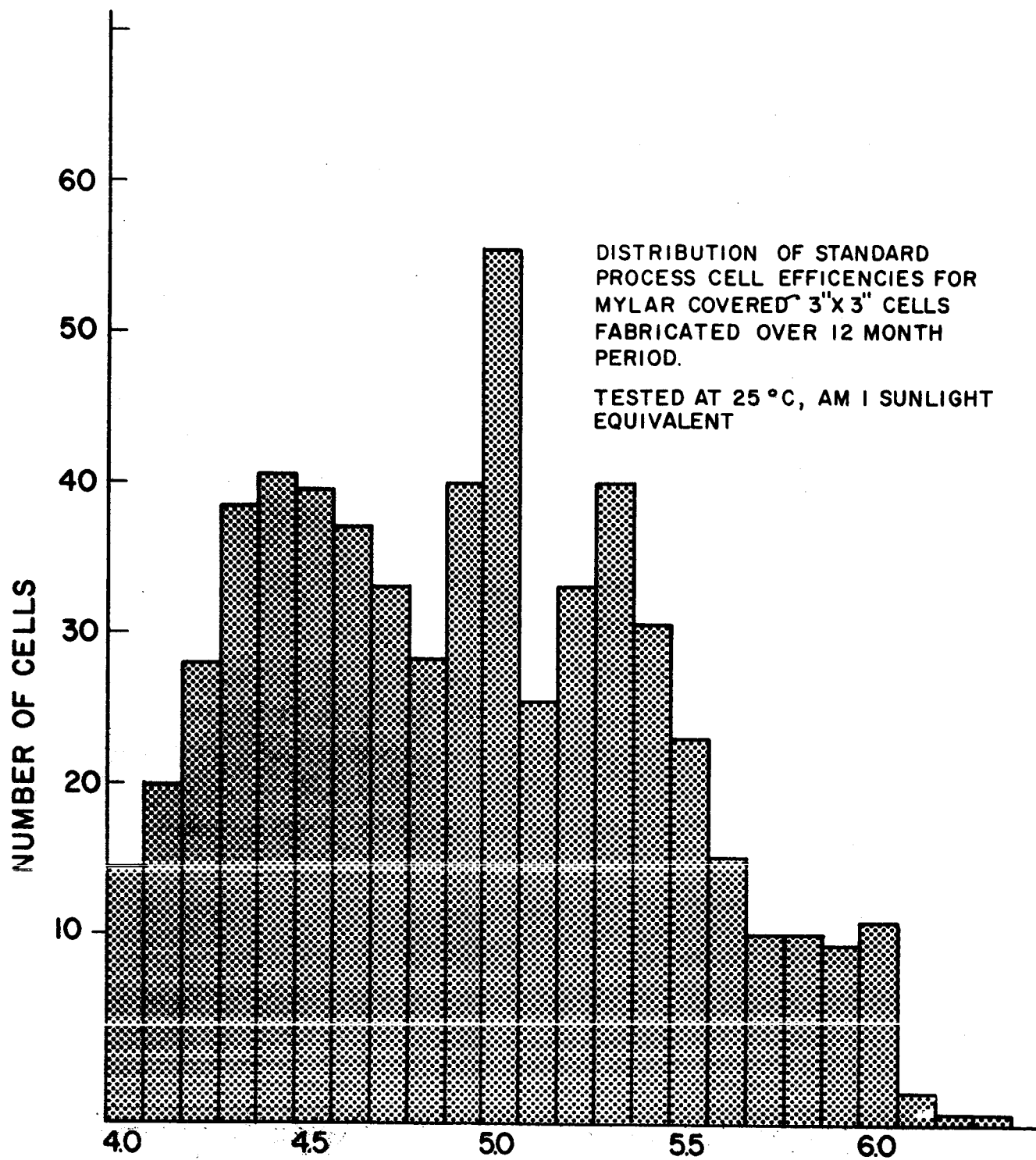


FIG. 3: STANDARD PROCESS CELL EFFICIENCIES - MYLAR CELLS.

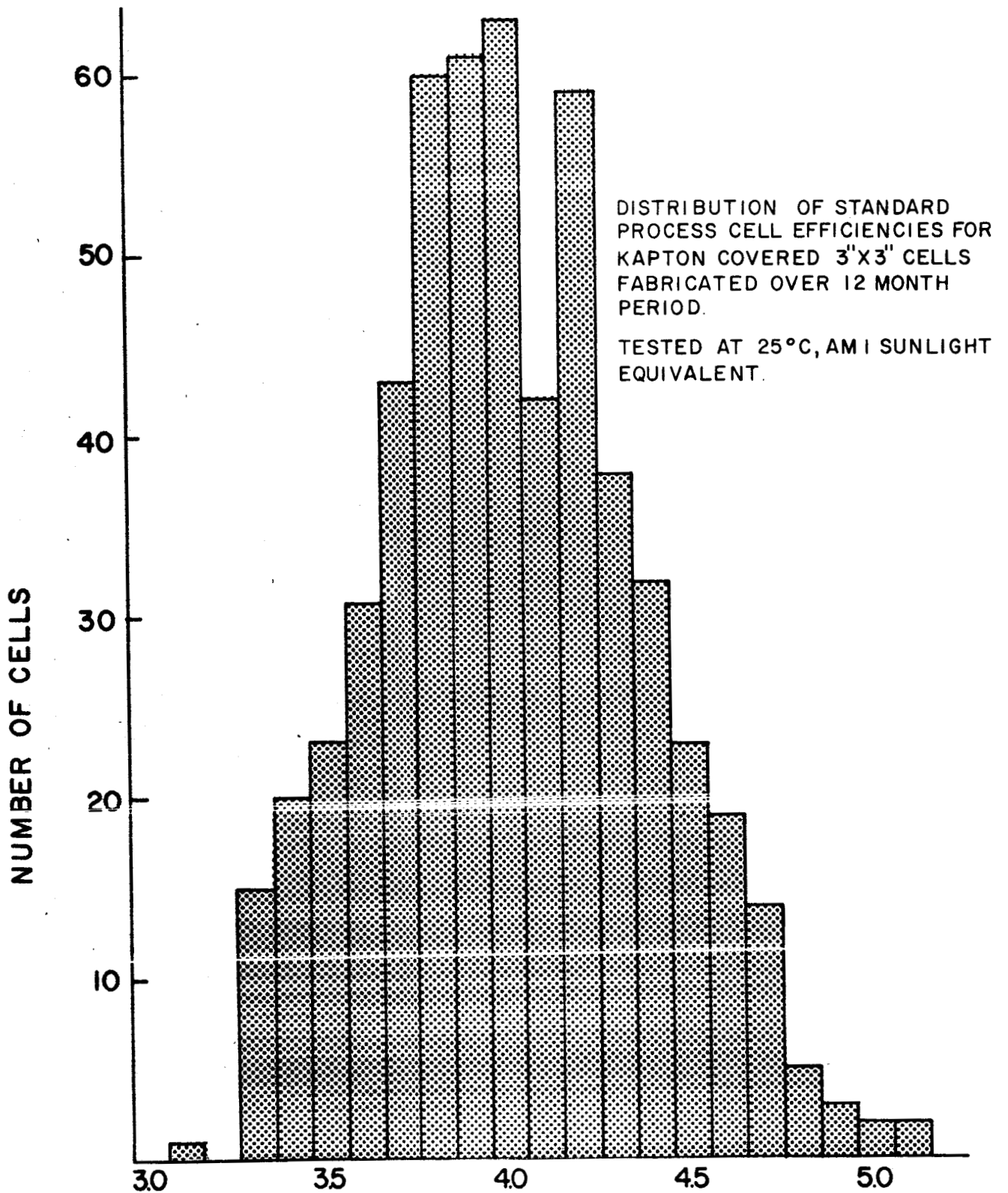


FIG. 4: STANDARD PROCESS CELL EFFICIENCIES - KAPTON CELLS.

III. STABILITY CHARACTERIZATION

The major task of this contract is to determine just how stable the present CdS thin film solar cell is, under the conditions that it would have to operate, and to improve the stability where needed. In order to accomplish this the design of the cell was fixed and the process for its fabrication was frozen and a degree of control and reproducibility was achieved. A number of cells were fabricated under these conditions and were evaluated for their stability under various test and storage conditions. Each month a minimum of 100 standard cells were fabricated and 75 of these were sent to NASA, Lewis Research Center, for thermal cycling and other space simulation tests. The balance was kept at Clevite for dry and wet shelf storage and for high temperature vacuum storage tests. While these tests are still continuing, the results to date are presented in the following paragraphs:

A. Dry Shelf Storage

Each month 4 standard process cells have been placed in a laboratory cabinet desiccator which is kept at room temperature. The cells are removed at monthly intervals thereafter and tested for their I-V characteristic curves under standard 25°C equivalent AM1 sunlight conditions. This test was started prior to the present contract, and Table II presents data on cells of the present design fabricated by the same process now being used, but prior to the present contract.

It can be seen that there is some variation in cell efficiencies as measured month by month. Most of this variation is attributed to variations in the calibration and accuracy of the standard test conditions, rather than to any change in the cells. Of the 22 cells with more than a year's dry shelf storage, only 5 show any real trend toward degradation of output. These cells are D296B, D304A, D344C, D381A and D410B. Of these, only 1 cell (D344C) appears to have degraded by more than 10%.

Table III gives the data on the dry shelf storage of those cells fabricated during the first six months of this contract. Of these, more than half show a real trend toward degradation of output. Most of these cells were fabricated in the period when much difficulty was experienced with the standard process line. The degradation on shelf storage in this period appears to be real and has also been noticed by Lewis Research Center on the cells shipped to them. It now appears that this degradation was caused by lack of control over the gold filled conductive epoxy cement used to attach the grids and over the clear epoxy cement used to attach the cover plastic.

Much of the trouble was from batches of epoxy which were over age at the time of use, but at least part of the problem was inadequate mixing and inadequate curing of the epoxies. Since the establishment of better controls over the incoming materials and over the fabrication process itself, the cells again appear to be holding up on shelf storage.

When the present design CdS thin film solar cell is properly made, there seems to be no measurable degradation on room temperature dry shelf storage over periods of 1-1/2 years or more. However, it is evident that adequate controls over the raw materials, component parts and fabrication process must be maintained in order to ensure shelf stable cells.

TABLE II
 DRY SHELF STORAGE - LONG TERM TEST DATA

Cell No.	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
	AM1, 25°C Efficiency after indicated number of months storage:																			
D289D	4.9	-	-	4.9	4.8	4.8	4.9	4.8	4.9	5.0	4.7	4.9	5.0	5.0	4.9	4.7	4.8	4.7	4.9	4.9
D292D	4.7	-	-	4.9	4.6	4.9	4.9	4.9	4.8	5.0	4.8	4.9	5.0	5.0	4.8	4.7	4.8	4.8	4.8	5.0
D296B	4.5	-	-	4.4	4.3	4.3	4.3	4.4	4.4	4.4	4.4	4.4	4.4	4.4	4.3	4.2	4.3	4.2	4.2	4.5
D304A	4.8	-	-	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.4	4.5	4.2	4.3	4.4	4.2	4.2	4.2	4.2	4.3
D306D	4.9	-	-	4.9	4.8	4.8	4.9	4.9	5.0	5.1	5.1	5.1	4.8	5.0	5.0	4.8	5.0	4.9	4.9	5.0
D315A	5.2	-	-	5.2	5.0	5.0	5.2	5.3	5.2	5.1	5.1	5.3	5.3	5.2	5.3	5.0	5.2	5.0	5.1	5.2
D336D	4.2	-	4.1	4.0	4.0	4.1	4.0	4.2	4.4	4.1	4.3	4.3	4.3	4.2	4.2	4.0	4.3	4.2	4.1	4.2
D344C	5.2	-	4.9	4.8	4.7	4.7	4.7	4.8	4.9	4.7	4.9	4.8	4.8	4.6	4.3	4.0	4.3	4.0	4.3	4.3
D355C	5.7	-	5.3	5.2	5.3	5.4	5.4	5.5	5.4	5.4	5.8	5.3	5.3	5.2	5.5	-	-	5.0	5.2	5.4
D364F	4.7	-	4.2	4.1	4.1	4.1	4.0	4.2	4.2	4.2	4.2	4.3	4.3	4.2	4.4	-	-	4.2	4.4	4.5
D375C	4.4	4.3	4.4	4.1	4.4	4.6	4.4	4.4	4.4	4.4	4.4	4.4	4.2	4.3	4.2	4.4	4.3	4.2	4.3	4.4
D381A	5.1	5.1	5.2	5.1	5.1	5.2	5.1	5.1	5.1	5.1	4.8	4.8	4.7	4.7	4.7	4.4	4.3	4.0	4.3	4.3
D385B	5.0	5.2	5.1	5.1	5.2	5.0	5.1	5.1	5.1	5.1	5.1	4.9	5.0	4.9	5.1	-	-	5.0	5.2	5.4
D386E	5.1	5.2	5.1	5.2	5.2	5.2	5.2	5.2	5.1	5.2	5.2	5.0	5.0	5.1	5.2	-	-	4.2	4.4	4.5
D391B	4.7	5.0	5.2	5.0	5.1	5.1	5.0	5.1	5.1	5.0	5.0	4.9	5.0	4.9	5.0	4.4	4.3	4.2	4.3	4.3
D395C	4.2	4.2	4.1	4.2	4.2	4.3	4.2	4.3	4.3	4.2	4.2	4.1	4.3	4.2	4.3	4.2	4.2	4.2	4.2	4.3
D403B	4.6	4.7	4.8	4.9	4.8	4.7	4.8	4.8	4.7	4.6	4.6	4.6	4.7	4.6	4.8	4.6	4.6	4.6	4.7	4.7
D410B	4.9	4.8	4.8	4.9	4.9	4.9	4.9	4.9	4.7	4.7	4.6	4.6	4.7	4.7	4.7	4.7	4.7	4.7	4.7	4.7

TABLE III

DRY SHELF STORAGE - SHORTER TERM TEST DATA

Cell No.	AM1, 25°C Efficiency after indicated number of months in storage:										
	0	1	2	3	4	5	6	7	8	9	10
D507F	5.7	5.3	5.3	5.1	4.9	4.9	4.7	4.7	off		
D513E	5.1	5.0	5.1	5.0	4.8	4.8	4.8	4.6	-	-	4.6
D521F	4.6	4.4	4.6	4.6	4.4	4.5	4.3	4.3	-	-	4.0
D522E	4.8	4.7	4.8	4.7	4.5	4.6	4.5	4.4	-	-	4.5
D551E	4.5	5.0	4.7	4.7	4.6	4.6	4.8	-	4.5		
D563A	4.8	4.9	4.6	4.6	4.5	4.6	4.7	-	4.5		
D579B	5.1	4.9	4.6	4.7	4.5	4.6	4.8	-	4.5		
D583C	4.8	5.0	4.7	4.7	4.6	4.6	4.8	-	4.5		
N14B2	5.5	5.2	4.8	4.8	4.7	4.7	-	-	4.6		
N14B5	4.4	4.1	3.8	3.9	3.8	3.8	4.0	off			
N20B1	4.9	5.1	4.8	4.8	4.7	4.9	5.0	-	4.6		
N31BK4	4.1	4.2	4.0	4.1	4.0	4.0	4.2	-	3.7		
D597E	5.0	4.4	4.4	4.3	3.9	4.5	off				
D609B	4.6	4.1	4.1	3.9	4.0	4.2	off				
N35B3	5.0	4.9	5.0	4.9	4.9	5.2	-	4.5			
N44B3	4.4	4.4	4.4	4.3	4.4	4.4	-	3.7			
N64BK5	4.0	4.0	4.1	4.1	-	-	4.0				
N65BK5	4.2	4.0	4.2	-	-	4.0					
N71AK2	4.1	3.8	4.0	4.0	-	-	3.9				
N78AK5	4.7	3.6	4.2	4.5	-	4.2					
N80AK6	4.2	-	3.8	4.0	-	3.9					
N85BK3	4.4	-	3.9	4.2	-	3.9					
N86C5	5.9	4.7	5.4	5.9	-	5.5					

B. Moisture Resistance

Earlier design CdS thin film solar cells were laminated using a Capran (nylon) adhesive to attach the cover plastic, and these cells were extremely sensitive to moisture degradation⁽⁵⁾. When epoxy cement was substituted for the nylon, it was found that the cells were affected only very slightly by moisture. Some cells experienced no drop in output after complete immersion in water for 8 weeks, and other cells showed a slight amount of degradation in 80% relative humidity storage for periods up to six months⁽⁶⁾.

Table IV gives the conversion efficiency data for those cells that have been on 80% relative humidity test for a year or more. As in the case of the dry shelf storage, there is a considerable amount of scatter to the data, but over and above the scatter there does appear to be a slow trend for degradation. In an effort to measure this trend more accurately, the data points for each cell were plotted on graph paper and a straight line drawn through the points as carefully as could be estimated by eye. The "corrected" values were picked off these graphs and are tabulated in Table V. These "corrected" values were then averaged to give the estimated degradation rate for 80% relative humidity room temperature storage.

An approximate average drop of 9% per year is indicated from these figures. On the basis of much less data a year ago it was estimated that the loss of output due to 80% relative humidity storage was probably less than 5% and more than 2% for a 12 week period. Thus the present data for a much longer period of time fixes the rate very close to the latter figure. However, the accuracy of this determination is still not high. There are some indications from a number of cells tested that much of the moisture degradation may occur in the first month or so and that the rate of degradation thereafter may be very much less. In some cases there actually appeared to be a definite though slight trend toward an increase in cell output during about the second quarter of the test. Of course, any degradation that might have occurred on dry shelf storage, due to faulty epoxies, etc., would presumably be included in these figures. Hence, we can say that the rate of output degradation due to 80% relative humidity storage is no more than 9% per year and is probably appreciably less.

In Table VI the data are presented on the wet shelf storage of those cells fabricated during the first six months or so of this contract on which six months or more data have been accumulated. As in the case of dry shelf storage, the degradation on these is more pronounced and is attributed more to the same lack of control over the cell fabrication process rather than to true moisture degradation. A number of these cells also show an initial increment of degradation well in excess of that which occurs subsequently.

It is planned to subject many of the cells which have shown degradation on wet shelf storage to a vacuum heat treatment in an effort to delineate how much of the drop in cell output is reversible and hence truly the result of moisture and not of other causes. There were very strong indications earlier that true moisture degradation in CdS cells is completely reversible unless the degradation affects the grid contact itself.⁽⁷⁾

TABLE IV

WET SHELF STORAGE - LONG TERM TEST-ORIGINAL DATA

Cell No.	AM1, 25°C Efficiency after indicated number of months storage:																		
	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
D137B	5.5	-	-	-	-	-	5.5	5.2	5.3	5.3	5.3	5.3	5.4	5.3	5.3	5.3	5.3	5.3	5.1
D291A	4.6	-	4.5	4.6	4.2	4.1	4.2	4.3	4.2	4.2	4.0	4.1	4.1	4.1	4.0	4.1	3.9	3.9	5.2
D294A	4.3	-	3.4	3.2	3.2	3.2	3.2	3.1	3.2	3.2	3.9	2.8	2.8	2.7					
D297C	4.6	-	4.4	4.3	4.0	4.2	4.2	4.2	4.3	4.4	4.2	4.3	4.3	4.3	4.2	4.4	4.2	4.3	4.3
D301A	4.6	-	4.3	4.3	4.0	4.0	4.2	4.2	4.2	4.2	4.1	4.1	4.1	4.1	3.9	4.0	3.7		
D313C	4.4	4.1	-	4.1	3.8	4.0	3.8	3.9	4.1	3.9	3.8	3.8	3.8	3.7	3.9	3.7	3.7		
D327A	2.8	2.9	-	3.0	2.7	2.8	2.8	2.8	2.7	2.7	2.7	2.6	2.8	2.8					
D348C	4.8	-	4.8	4.2	4.3	4.4	4.4	4.5	4.4	4.2	4.5	4.6	4.4	4.4	4.6	4.4	4.4	4.6	4.5
D350F	4.8	-	4.8	4.5	3.8	4.0	4.0	4.2	4.4	3.7	4.3	4.2	4.2	4.2	4.4	4.2	4.3	4.3	4.4
D350C	4.3	4.3	4.4	4.2	4.3	4.4	4.5	4.5	4.2	4.4	4.4	4.2	4.4	4.1	4.2	4.2	4.2	4.2	4.4
D357E	4.4	4.3	4.5	4.4	4.3	4.4	4.4	4.3	4.3	4.3	4.3	4.1	4.3	4.0	4.1	4.0	4.1	4.1	4.1
D372A	4.5	4.3	4.3	4.3	4.3	4.2	4.2	3.9	4.0	4.2	4.2	4.0	4.3	4.0	4.0	4.0	4.0	4.0	4.1
D378B	4.8	4.6	4.6	4.5	4.5	4.4	4.4	4.3	4.3	4.5	4.5	4.0	4.4	4.0	4.1				
D385F	5.1	5.2	5.0	5.0	5.1	4.8	4.7	4.8	4.7	4.3	4.6	4.3	4.4	4.8	4.7				
D401B	5.2	5.0	5.0	5.0	5.0	4.8	4.7	4.7	4.8	4.7	5.0	4.6	4.8	4.8	4.7				
D405A	4.8	4.5	4.6	4.5	4.5	4.4	4.4	4.4	4.3	4.5	4.3	4.4	4.4	4.4	4.4				
D411F	4.6	4.4	4.4	4.4	4.3	4.3	4.3	4.3	4.2	4.4	4.0	4.3	4.3	4.3	4.3				
D424B	4.5	4.4	4.5	4.3	4.4	4.3	4.3	4.3	4.4	4.1	4.0	4.2	4.2	4.2	4.2				
D424F	5.6	2.8	5.3	5.2	5.3	5.2	5.1	5.1	5.3	5.0	5.0	5.1	5.1	5.1	5.1				
D454A	5.2	4.6	4.6	4.5	4.4	4.4	4.3	4.2	4.0	4.0	3.9	3.9	4.1	-	3.6				

TABLE V
WET SHELF STORAGE - LONG TERM TEST - CORRECTED DATA

Cell No.	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
	AM1, 25°C Efficiency after indicated number of months storage:																			
D187B	5.5	5.5	5.5	5.5	5.4	5.4	5.4	5.4	5.4	5.3	5.3	5.3	5.3	5.3	5.3	5.2	5.2	5.2	5.2	
D291A	4.6	4.5	4.5	4.5	4.4	4.4	4.4	4.3	4.3	4.3	4.2	4.2	4.2	4.1	4.1	4.1	4.0			
D294A	3.6	3.5	3.4	3.4	3.3	3.3	3.2	3.1	3.1	3.0	3.0	2.9	2.8	2.8	2.8					
D297C	4.4	4.4	4.4	4.4	4.4	4.4	4.4	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.2	4.2	4.2	4.2	
D301A	4.4	4.4	4.4	4.3	4.3	4.3	4.2	4.2	4.2	4.1	4.1	4.1	4.0	4.0	4.0	3.9	3.9	3.9	3.9	
D313C	4.2	4.2	4.2	4.1	4.1	4.1	4.0	4.0	3.9	3.9	3.9	3.8	3.8	3.8	3.7	3.7	3.6			
D327A	2.9	2.9	2.9	2.9	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.7	2.7	2.7	2.7					
D348C	4.7	4.6	4.6	4.6	4.6	4.6	4.6	4.5	4.5	4.5	4.5	4.5	4.5	4.4	4.4	4.4	4.4	4.4	4.3	
D350F	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	
D350C	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3	
D357E	4.5	4.5	4.5	4.4	4.4	4.4	4.4	4.3	4.3	4.3	4.2	4.2	4.2	4.1	4.1	4.1	4.1	4.1	4.1	
D372A	4.4	4.4	4.4	4.3	4.3	4.3	4.2	4.2	4.2	4.2	4.1	4.1	4.1	4.1	4.0	4.0	4.0	4.0	4.0	
D378B	4.7	4.6	4.6	4.5	4.5	4.4	4.4	4.3	4.3	4.2	4.2	4.1	4.1	4.0	4.0					
D385F	5.2	5.1	5.1	5.0	4.9	4.9	4.8	4.7	4.7	4.6	4.5	4.5	4.4	4.4	4.4					
D401B	5.2	5.1	5.1	5.0	5.0	4.9	4.9	4.8	4.8	4.7	4.7	4.6	4.6	4.5	4.5					
D405A	4.7	4.6	4.6	4.6	4.5	4.5	4.5	4.5	4.4	4.4	4.4	4.4	4.3	4.3	4.3					
D411F	4.5	4.4	4.4	4.4	4.3	4.3	4.3	4.3	4.2	4.2	4.2	4.2	4.1	4.1						
D424B	4.5	4.4	4.4	4.4	4.3	4.3	4.3	4.3	4.2	4.2	4.2	4.2	4.1	4.1						
D424F	5.4	5.3	5.3	5.3	5.2	5.2	5.2	5.1	5.1	5.1	5.1	5.1	5.0	5.0						
D454A	4.7	4.7	4.6	4.5	4.4	4.4	4.3	4.2	4.1	4.1	4.0	3.9	3.8	3.8	3.7					
AVG	4.53	4.48	4.47	4.43	4.39	4.37	4.34	4.30	4.27	4.24	4.21	4.18	4.14							

TABLE VI

WET SHELF STORAGE - SHORTER TERM TEST DATA

Cell No.	AM1 - 25°C Efficiency after indicated months of Wet Storage:											
	0	1	2	3	4	5	6	7	8	9	10	11
D436E	5.3	4.7	4.6	4.6	4.5	4.3	4.3	4.3	4.2	4.4	-	4.1
D450C	5.3	4.2	4.1	4.3	4.3	4.0	4.0	4.1	3.8	3.8		
D454E	5.3	4.1	-	-	-	3.7	3.7	3.5	3.6	3.7		
D480B	5.1	4.6	4.5	4.7	4.4	4.3	4.3	4.3	4.1	4.4	-	4.0
D495A	5.4	4.8	4.7	4.7	4.5	4.5	4.5	4.5	4.5	4.7	-	4.3
D487C	5.5	5.1	5.0	5.1	4.8	4.8	4.8	4.8	4.7	5.0	-	4.5
D476A	5.0	4.8	4.7	4.8	4.6	4.5	4.5	4.5	4.1	4.7	-	4.3
D506B	5.7	-	5.9	4.9	4.8	4.7	4.8	4.9	-	4.5		
D509E	5.5	-	4.8	4.4	4.4	4.3	4.3	4.4	-	4.0		
D516A	5.3	-	4.6	4.4	4.4	4.3	4.2	4.5	-	4.1		
D526C	4.4	-	3.9	3.8	3.8	3.8	3.8	4.0	-	4.7		
D554A	5.7	5.4	5.0	-	4.9	5.0	5.2	-	4.6			
D562E	4.7	4.2	3.9	3.9	3.8	3.7	3.8	-				
N14B8	5.0	5.1	4.7	4.7	4.7	4.6	5.0	-	4.5			
D580E	5.0	4.3	4.0	4.1	3.9	4.0	4.1	-	3.7			
D585C	5.1	5.1	4.7	4.7	4.5	4.5	4.7	-	4.2			
N17B3	4.8	4.6	4.2	4.3	4.1	4.0	4.1	-	3.6			
D602D	4.6	3.2	4.0	3.9	4.0	4.1						
D615C	5.3	4.9	5.0	4.8	4.8	5.1	-	4.5				
N38B7	4.6	4.1	4.2	4.1	3.9	4.0	-	4.8				
N51B8	5.3	4.4	4.8	4.6	4.6	4.8	-	4.2				
N52B4	4.9	4.7	4.5	4.6	-	4.5	3.9					
N59BK7	3.4	3.2	3.6	3.5	-	3.7	3.7	3.7	-	3.6		

C. High Temperature Storage

1. Storage at 100°C, 10⁻⁴ Torr

Each month 4 standard process cells were placed on storage in a vacuum oven held at 100°C at 10⁻⁴ Torr. The cells were in the dark in open circuited condition. They were removed periodically and tested under standard 25°C air mass 1 equivalent sunlight conditions and then returned to the vacuum oven. The data on those cells which have been on this test for 8 months or more are presented in Table VII.

As in the case of the humidity and the dry shelf storage tests, there are wide variations between cells, and these variations are attributed to accidental causes arising from incomplete control over the fabrication process. As before, the group of cells showing best performance on this test are more likely than the others to be indicative of the intrinsic degradation under the test conditions.

The best performance was obtained from a group of 4 cells which were fabricated in 1966 and which have been on test for more than a year. These were cells D379E, D388F, D392A and D401F. The output of each of these cells as read monthly was plotted on a graph and a smooth curve was drawn to correspond to these points as closely as possible by visual estimation. These curves were not straight lines as in the case of the moisture test. Rather they were linear for the first few months holding their initial level, then dropped steadily for the next 4 to 6 months, and then dropped more rapidly.

Table VIII gives the "corrected" smooth curve values for these 4 cells and the average value has been calculated for each month of 100°C vacuum storage. The drop in average cell output for these best 4 cells was just 10% after the first 8 months, and an additional 12-1/2% over the following 4 month period.

In Table IX are presented the data on the 100°C vacuum storage of more recently fabricated cells, which have less than 8 months accumulated data. The behavior of many of these cells was very poor on the vacuum thermal storage test, and the worst data was on those cells made in the period when most of the difficulty with poor process control was experienced. On several cells in this grouping a very erratic behavior was recorded with the output dropping and then rising much more than can be accounted for by the inaccuracies of measurement and calibration. Cells D463C, D462A, D481C, D532D and D574D exhibited this intermittency. It seems probable that this erratic behavior may be caused by internal intermittent contacts, at cracks or delaminations, because comparable behavior was noted on some cells on thermal cycling tests. This will be discussed in more detail later in this report.

2. Storage at 150°C

The purpose of the higher temperature vacuum storage test is to accelerate those degradation effects which otherwise might take too long a time to become evident. A number of cells from each month's standard production, and a number of selected experimental cells, have been put on this test. The test consists of storage in an oven at 150°C in a vacuum of 10⁻⁴ Torr with the cells lightly clamped between glass plates. The cells are removed weekly, tested under standard temperature and pressure conditions, and then returned to the vacuum oven.

TABLE VII
100°C VACUUM STORAGE - LONGER TERM DATA

Cell No.	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
	AM1, 25°C Efficiency after indicated months:															
D349A	4.0	4.8	4.6	4.5	3.8	3.3	2.9	2.6	2.3	2.1	1.5	1.0	0.7	0.7	off	
D357B	4.3	4.0	3.4	2.8	1.2	0.9	0.3	off								
D357C	4.8	3.8	1.7	-	0.3	0.2	0.2	0.3	0.4	0.3	0.2	0.1	0.1	0.2	off	
D363E	3.3	3.0	3.0	2.9	2.0	1.8	1.0	0.9	1.0	1.0	0.5	0.2	0.2	0.2	off	
D369E	4.9	4.6	4.6	4.4	4.5	4.3	4.1	3.8	3.5	2.5	2.1	1.7	1.0	off		
D373C	4.1	3.9	3.9	3.6	3.8	3.7	3.6	3.5	3.4	3.1	3.0	2.6	2.4	off		
D377A	5.0	4.7	4.7	4.2	4.1	3.6	3.2	2.6	1.6	0.5	0.4	0.5	0.4	off		
D379E	5.1	5.2	5.2	5.0	5.1	5.0	4.9	4.7	4.7	4.6	4.3	4.3	4.0	3.8	3.7	off
D385E	4.7	4.5	4.3	4.2	4.2	4.0	3.8	3.7	3.8	3.4	3.3	3.2	off			
D388F	4.6	5.0	4.8	4.9	4.9	4.6	4.5	4.4	4.4	4.2	4.2	4.0	3.8	3.9		
D392A	5.0	5.3	5.0	5.1	5.0	4.8	4.7	4.5	4.5	4.5	4.4	4.3	4.1	4.1		
D401F	4.5	4.7	4.6	4.7	4.8	4.5	4.5	4.5	4.5	4.0	3.6	3.5	3.7	4.0		
D403D	6.0	5.7	5.5	4.2	3.4	1.9	1.3	1.3	short	off						
D405C	5.6	5.6	5.5	4.6	4.9	4.4	4.2	4.2	3.4	3.6	3.2	off				
D407D	4.9	3.1	3.0	2.5	2.8	2.7	4.0	4.0	3.7	4.0	3.7	3.5	3.3			
D411D	5.0	4.4	4.2	3.4	3.3	2.3	1.7	1.7	0.9	off						
D438D	5.6	5.8	5.6	5.7	5.5	4.8	4.3	-	3.9							
D462E	6.1	5.8	5.7	5.7	5.8	5.3	5.7	-	5.1							
D504E	5.6	5.7	5.5	5.5	5.3	5.1	4.5	4.6	-	4.2						
D514E	5.3	4.8	4.6	4.6	4.5	4.4	4.0	4.3	-	3.9						

TABLE VIII

100°C VACUUM STORAGE - CORRECTED DATA - 4 BEST CELLS

Cell No.	AM1, 25°C Efficiency after indicated months:														
	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
D379E	5.2	5.2	5.2	5.1	5.1	5.0	4.9	4.8	4.7	4.5	4.4	4.2	4.1	3.9	3.7
D388F	5.0	5.0	5.0	4.9	4.9	4.8	4.7	4.6	4.5	4.3	4.2	4.0	3.9	3.7	
D392A	5.1	5.1	5.0	5.0	5.0	4.9	4.8	4.7	4.6	4.5	4.4	4.3	4.2	4.1	
D401F	4.8	4.8	4.7	4.7	4.6	4.6	4.5	4.4	4.3	4.2	4.0	3.8	3.5	3.3	
Avg.	5.03	5.03	4.98	4.93	4.90	4.83	4.73	4.63	4.53	4.38	4.25	4.08	3.93	3.73	

TABLE IX

100°C VACUUM STORAGE - MORE RECENT CELLS

Cell No.	AM1, 25°C Efficiency after indicated months:								
	0	1	2	3	4	5	6	7	8
D455D	5.9	5.0	4.5	4.3	3.9	3.1	2.0	off	
D462A	5.9	5.0	4.9	3.4	3.8	4.6	3.3	off	
D463C	5.3	3.6	2.8	4.5	1.5	0.9	0.5	off	
D481C	5.2	4.9	4.6	2.9	4.3	3.7	3.7	3.4	
D484B	6.1	5.3	4.5	4.7	1.7	0.9	0.4	off	
D485E	5.3	5.0	4.7	4.7	4.7	4.2	4.2	4.0	off
D518F	4.7	4.7	4.4	4.3	3.6	3.1	2.4	2.0	off
D526B	4.3	4.2	4.1	4.0	3.8	3.5	3.0	off	
D532D	4.3	2.0	2.9	1.7	1.5	off			
D554E	5.4	5.4	5.1	5.1	5.2	-	4.6		
D568E	4.5	4.9	4.5	4.4	4.5	off			
D574D	5.6	3.5	4.3	4.4	4.5	off			
D579F	5.0	4.7	4.6	4.5	4.6	-	4.3		
D580B	5.3	5.1	4.9	4.9	4.9	-	4.5		
D588DK	3.8	3.7	3.4	3.1	2.1	off			
H108A4	5.0	5.3	-	5.3	5.3	-	5.0		
H108A5	5.0	5.3	-	5.2	-	5.0	-		
H108B2	4.9	5.0	-	5.0	5.0	-	4.7		
H108B5	5.1	5.3	-	5.0	5.3	-	5.0		

Nearly all of the standard construction cells have failed on this test within a week or two. The better performance records are summarized in Table X. Again, it is assumed that the better performing cells are more nearly representative of the intrinsic behavior of the cells on this test and that the more rapidly deteriorating cells are faulty in their construction. It is seen that there are some signs of erratic outputs even among these better cells.

A few cells have held up for 4 weeks at 150°C with 10% or less degradation, and several more with 20% or less. The degradation in these cases is characterized by a loss of fill factor due to a major increase in the series resistance. The best performance on this test was from some of the cells with evaporated aluminum interlayers in place of the electroplated zinc, and with a molybdenum substrate cell. Further tests of these experimental variations are being planned.

In another experiment, 4 ungridded open cells were placed in the 150°C vacuum oven and held there for 7 weeks, and then removed and gridded, laminated and tested. These were given Kapton covers and were fabricated from a lot of cells which had been giving about 4.1 to 4.2% average conversion efficiency. These 4 cells when first tested gave efficiencies of 2.7, 2.9, 2.0 and 2.3%. That is, they gave about 60% of their expected output after 7 weeks at 150°C. The I-V curves for these cells were quite similar to those of cells which had been exposed to the 150°C storage after gridding. Thus, it is concluded that such degradation on this test is not a case of grid contact loosening.

It is assumed that there probably is an inherent degradation at this temperature due to a diffusion of impurities in the insulating layer that would cause an increase in the thickness of this i-layer. Such a change should be characterized by a marked decrease in the junction capacitance and a marked increase in the internal series resistance. Though it is difficult to measure the capacitance of the junction of these large area cells - due to shunt leakage paths, etc. - such marked changes in capacitance have indeed been measured.

A number of standard 3" x 3" cells were tested for their conversion efficiency under standard conditions, their reverse bias breakdown voltage (i. e., the reverse bias required to cause 5.0 ma of current to flow) and their capacitance. The cells were stored in the 150°C vacuum oven for 3 days and the measurements were repeated. Then they were stored for another 8 days and again measured. Table XI gives the data for the better cells on this test.

As can be seen the reverse breakdown voltage varied mostly between about 2 and 3 volts initially, and in most cases this increased with 150°C storage. The capacitance readings showed more scatter, due undoubtedly to the very uneven topology of the CdS film surface and to various flaws in the films, and in every case decreased appreciably with heating. (Capacitance readings were not attempted after 11 days heating because of the difficulties in making the measurement.)

The decrease in capacitance with heating is commensurate with the concept of an insulating region in the CdS, adjacent to the Cu_2S layer, caused by compensation of donors by diffusion of Cu^+ ions. Heating would increase the penetration of the Cu^+ ions and hence the thickness of the insulating region. The increase in the reverse breakdown voltage would also fit in with this concept since the increasing size insulating region would increase the resistance of various shorting paths along grain boundaries and other structural flaws.

TABLE X
150°C VACUUM STORAGE

Cell No.	AM1, 25°C Efficiency after indicated weeks:						Remarks
	<u>0</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	
D527A	4.0	3.6	3.6	3.3	2.0		std
D527B	4.0	3.6	3.7	3.4	3.2	3.0	std
N81AK3	4.1	3.9	3.5	2.8	3.2	3.2	std
N84C3	5.0	4.4	3.7	3.1	2.8	2.8	std
N85A2	5.5	4.7	4.5	4.3	4.1	3.7	std
N87C2	5.3	4.6	3.5	3.7			std
N87C3	5.7	4.0	2.7				Annealed Cu Grid - Au plated
N87C8	5.8	3.9	3.5				Solid Gold Grid
A981C	4.7	5.0	4.9	4.8	4.5		Al Interlayer
A981D	4.3	4.6	4.2	4.0	3.5	2.4	Al Interlayer
A997A	4.6	4.6	4.6	3.7			Al Interlayer
A981A	4.9	5.0	5.1	4.9	4.2	3.3	Al Interlayer
A997D	4.7	4.0	3.9	3.7			Al Interlayer
B439F	4.0	3.8	3.9	3.8	3.5	3.5	Moly Substrate
A970D	5.9	5.7	5.1	3.7	2.1		Copper Substrate (zinc plated)

TABLE XI

EFFECT OF 150°C VACUUM STORAGE ON EFFICIENCY,
CAPACITANCE AND DARK DIODE CHARACTERISTIC

Cell No.	Initial		3 days @ 150°C		11 days @ 150°C	
	Breakdown Voltage (v)	Capac. Eff. %	Breakdown Voltage (v)	Capac. Eff. %	Breakdown Voltage (v)	Capac. Eff. %
N108BK5	2.4	6.85	3.6	1.86	7.4	3.7
N108BK6	2.2	3.91	3.8	2.26	7.0	3.5
N108BK7	2.5	3.72	3.0	1.42	2.0	4.0
N108BK9	2.0	3.81	3.0	1.68	5.0	3.7
N108CK4	2.8	1.20	6.0	.67	10.0	3.6
N108CK5	2.4	1.86	6.0	.45	0.0	4.0
N110BK1	2.0	4.15	2.4	2.60	5.0	3.7
N110BK2	2.0	4.53	2.8	3.13	5.0	3.7
N110BK3	1.5	1.78	0.0	-	0.5	3.6
N110BK4	2.5	4.22	2.5	-	5.0	3.7
N110BK5	2.3	3.70	5.0	2.61	10.0	3.7
N110BK7	1.6	2.67	2.0	1.32	6.0	3.7
N110BK8	2.4	2.69	4.8	1.09	6.0	3.7
N110BK9	3.4	1.44	0.0	-	0.4	3.8
N111BK4	2.0	3.63	4.0	1.14	3.0	3.7
N111BK5	2.2	5.23	4.5	1.22	7.0	3.6
N111CK5	2.2	2.18	5.0	0.53	4.0	3.4
N111CK8	2.4	1.77	1.0	0.60	1.5	3.6
N112AK1	2.4	1.52	0.0	-	0.1	3.7
Avg.	2.3	3.20	3.1	1.19	4.5	3.69

Capacitance not measured

The thicker insulating layer however would have undesirable effects since it would increase the internal resistance of the cell and hence reduce cell efficiency. The efficiency, of course, is reduced and the reduction is marked by very severe increases in the series resistance as evidenced by the change in the slope of the I-V characteristic as it crosses the voltage axis.

D. Thermal Cycling

There has been a long history of thermal cycling tests on CdS thin film solar cells, with a wide variety of different results being obtained. The first Clevite high efficiency (4 to 5%) CdS thin film cells were formed on molybdenum metal substrates. The first batch of these that were delivered to the Chemistry and Energy Conversion Division of the NASA Lewis Research Center were placed on their internal temperature cycling test. The cells withstood more than 3000 cycles between about -60°C and $+60^{\circ}\text{C}$ without any failures⁽⁸⁾.

The next batch of these same design cells however gave very erratic results on temperature cycling. Most of them failed within a few hundred to a few thousand cycles. The cause of failure was believed to be a loosening of the grid contact. The grids at that time were held in pressure contact to the barriers by the cover plastic which was laminated to the cell with a thermoplastic (nylon) adhesive. The temperature of the lamination process was very critical and in spite of several months of efforts the conditions of the first batch of cells could not be duplicated. Further, it appeared that the conditions of the Lewis Laboratory thermal cycling test were not as severe as those of similar facilities at the Boeing Company in Seattle, as none of the cells tested on the Boeing facility held up.

For these and for other reasons the thermoplastic cover adhesive was replaced with a clear epoxy cement, and a conductive silver epoxy cement was used to attach the grid. However, these cells also failed on thermal cycling test, but in a different way. When the cells were removed from the vacuum chamber, and tested a few days later under standard conditions, they exhibited no degradation at all. It was finally determined that the silver in the conductive epoxy caused a temporary degradation of cell output after heating and that at room temperature this degradation would anneal out. The mechanism of this effect was never really determined, but it was found that the use of gold in place of the silver eliminated it.

However, the first cells made with a conductive gold epoxy grid cement also failed on vacuum thermal cycling test. In this case the failures were catastrophic and the cells generally did not recover, though in a few cases the cell output would come and go in a haphazard manner. The failures were due to internal short circuits, a few of which were intermittent. For those few cells returned to Clevite for analysis, the cause of the short circuits was found to be pinholes in the CdS film. These pinholes resulted from spattering of CdS particles onto the substrates during CdS film evaporation. They were essentially eliminated by better process control of the evaporation step, and by better inspection techniques to reject CdS films containing pinholes.

This is where the CdS thin film solar cell stood at the beginning of the present contract. Four groups of thermal cycling tests have been run on Clevite cells in this 1967 contract period and the results of these are detailed below:

1. Boeing Test - NASA, Lewis Contract - April 1967 Production Cells

The cells were plastic substrate cells with Mylar cover plastic overcoated with clear Pyre-ML. They were otherwise made by the same process that has been in use through the entire period of this contract. However, the CdS films were evaporated in the small vertical evaporator and the degree of process control was minimal. Table XII summarizes the initial test data on these cells measured at Clevite just prior to shipment to NASA.

At the time it was evident that these cells were of poor quality. Many of them had dropped in output by as much as 10% in the 1 to 2 week period after fabrication. Several cells were wrinkled or chipped and the fill factors were generally poor - due to poor shunt characteristics. However, these were all that were available in the April monthly period, and hence were forwarded to NASA as per the contract requirement.

After checking at Lewis Research Center, NASA, the cells were forwarded to the Boeing Company, Space Division, in Seattle for thermal cycling test. The tests were conducted in a clean vacuum chamber with the pressure at all times below 10^{-6} Torr. The walls of the chamber were black and cooled with liquid nitrogen. Each test cycle consisted of a 60 minute exposure to light followed by a 30 minute period of darkness. The cell temperatures alternated from about -70°C to about $+70^{\circ}\text{C}$. Cell performance was measured at periodic intervals with a light source which simulated AM0 sunlight.

After 300 cycles the maximum power outputs had dropped to between 52 and 82% of their initial values with most of the degradation occurring in the first 100 cycles. After 368 cycles the vacuum chamber was brought to room temperature and filled with dry nitrogen. The output of some of the cells recovered partially. Table XIII gives the values of the corrected maximum cell outputs at various stages of this test.

While there were wide variations in behavior of this group of cells on temperature cycling, in general they were characterized by an increasingly worsening fill factor, with the I-V curve in some cases becoming a straight line. Also, as the number of cycles increased, a different I-V curve would be traced in one direction than in the opposite direction. This is illustrated in Figure 5. In other cases very erratic I-V curves would be traced, as illustrated in Figure 6.

Several of these cells, when returned to Clevite after the completion of the test, were delaminated at the edges of the cells. The delamination was generally between the CdS layer and the conductive substrate and may have extended inward from each side edge as much as 3 to 5 mm at the middle of each edge.

2. Boeing Test - Lincoln Lab Contract - July 1967 Production Cells

These were also plastic substrate cells, but with Kapton cover plastic. Somewhat better control had been exercised over the production process and a much more rigorous inspection was imposed. Further, the cells were held for several months to ensure that there was no tendency to degrade on shelf storage and the cells were deliberately subjected to several alternate periods of deep freeze and vacuum oven storage in order to weed out cells that were likely to fail rapidly. A number of such cells were in fact so weeded out.

TABLE XII

CLEVITE TEST DATA ON CELLS USED FOR BOEING
THERMAL CYCLING OF APRIL 1967 PRODUCTION

<u>Cell No.</u>	<u>OCV</u>	<u>SCC</u>	<u>Vmp</u>	<u>Imp</u>	<u>M. P.</u>	<u>F. F.</u>	<u>Eff.</u>	<u>Remarks</u>
D533E	.465	.855	.350	.705	.245	61	4.5	Bad shunt
D534B	.465	.900	.345	.730	.250	60	4.6	Bad shunt
D535D	.460	.910	.357	.770	.257	64	4.9	Void & patch
D536A	.465	.860	.360	.755	.270	67	5.0	Chipped
D536C	.465	.835	.360	.730	.260	67	4.8	Degrading
D537D	.470	.900	.345	.745	.260	61	4.8	Degrading
D537E	.465	.925	.360	.745	.270	63	4.9	Bad shunt
D545A	.470	.840	.345	.680	.235	60	4.3	Degrading
D557A	.465	.850	.345	.670	.230	57	4.2	Bad shunt Degrading

Mylar Covered Cells with Pyre-ML Overspray

Tested at 25°C in Equivalent AM 1 Sunlight

TABLE XIII

BOEING THERMAL CYCLING DATA ON APRIL 1967 CELLS

Cycle No.	Max. Power in mW for indicated Cell Numbers:									Avg.
	D557A	D545A	D537E	D537D	D536C	D536A	D535D	D534B	D533E	
0	148	150	99	125	208	204	188	161	153	160
10	118	137	66	120	204	192	178	146	131	144
20	119	126	65	118	195	185	181	136	115	138
30	86	110	63	119	155	146	160	103	104	116
41	83	97	57	115	144	137	146	117	98	110
50	89	88	72	113	127	121	138	106	86	104
60	93	97	54	108	135	123	137	119	105	108
70	93	95	51	108	128	128	131	113	102	105
80	88	92	48	109	120	128	124	103	108	102
90	86	90	48	102	136	114	121	95	100	99
100	83	92	52	99	129	124	118	104	102	100
130	77	87	46	98	98	100	106	97	99	90
161	79	86	48	94	126	114	123	97	93	96
190	91	95	50	102	134	124	116	108	93	101
223	102	97	50	104	127	123	126	98	93	102
257	88	97	47	98	122	104	121	102	87	96
287	89	89	49	104	106	109	114	100	86	94
300	89	91	52	102	126	118	115	96	94	98
368*	80	88	82	90	146	127	132	118	118	109
368**	82	90	61	89	144	111	123	116	112	103
368***	114	106	71	102	155	116	115	142	147	119

*Cells in Dry N₂ at one atmosphere for 1 hour.

** Cells in Dry N₂ at one atmosphere for 2 days.

*** Cells out of Tank on 60° Temp. Controlled Block.

Measured at temperature (approx. 70°C) at AM0.

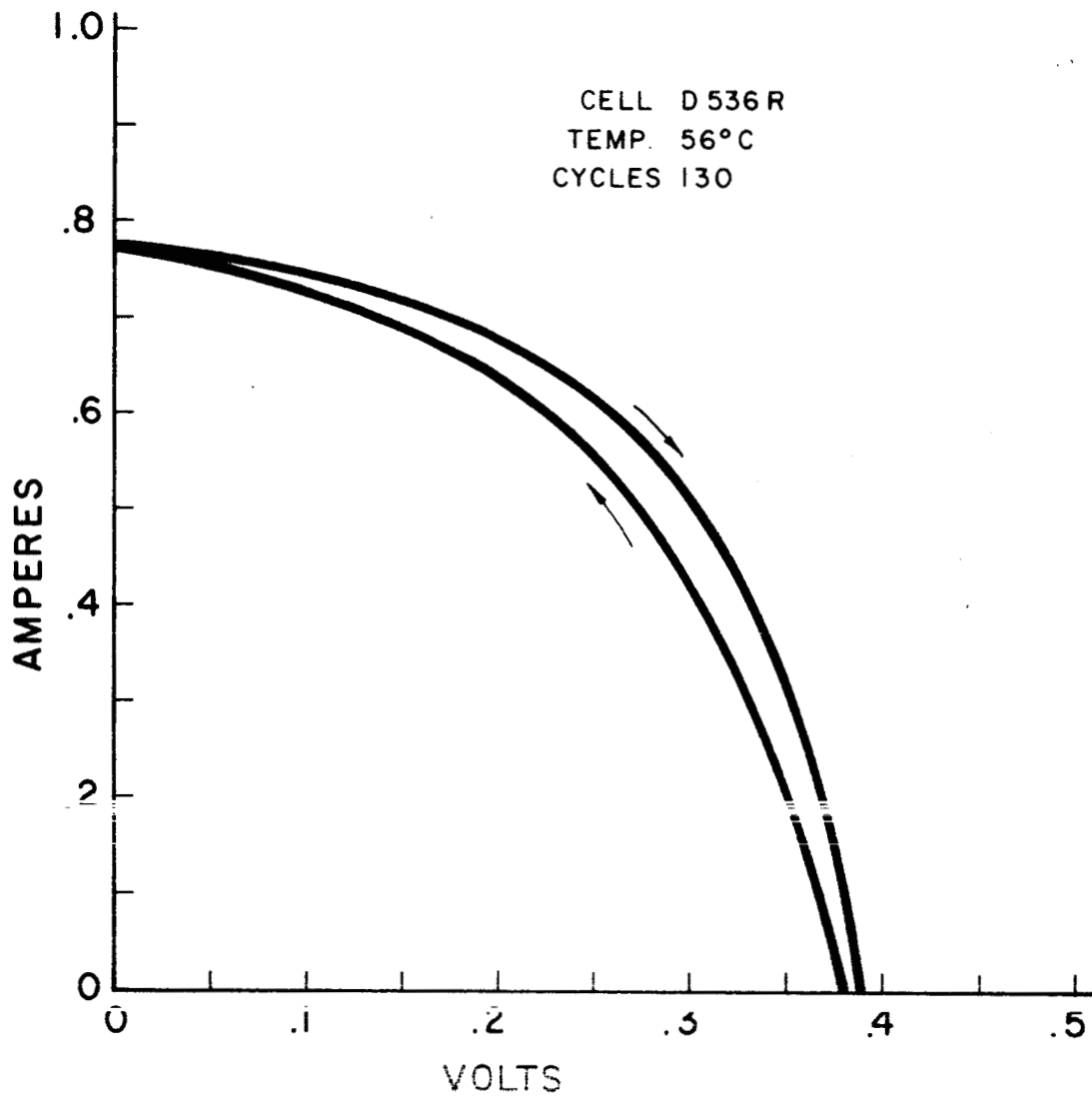


FIG. 5: HYSTERESIS EFFECT ON BOEING THERMAL CYCLING TEST.

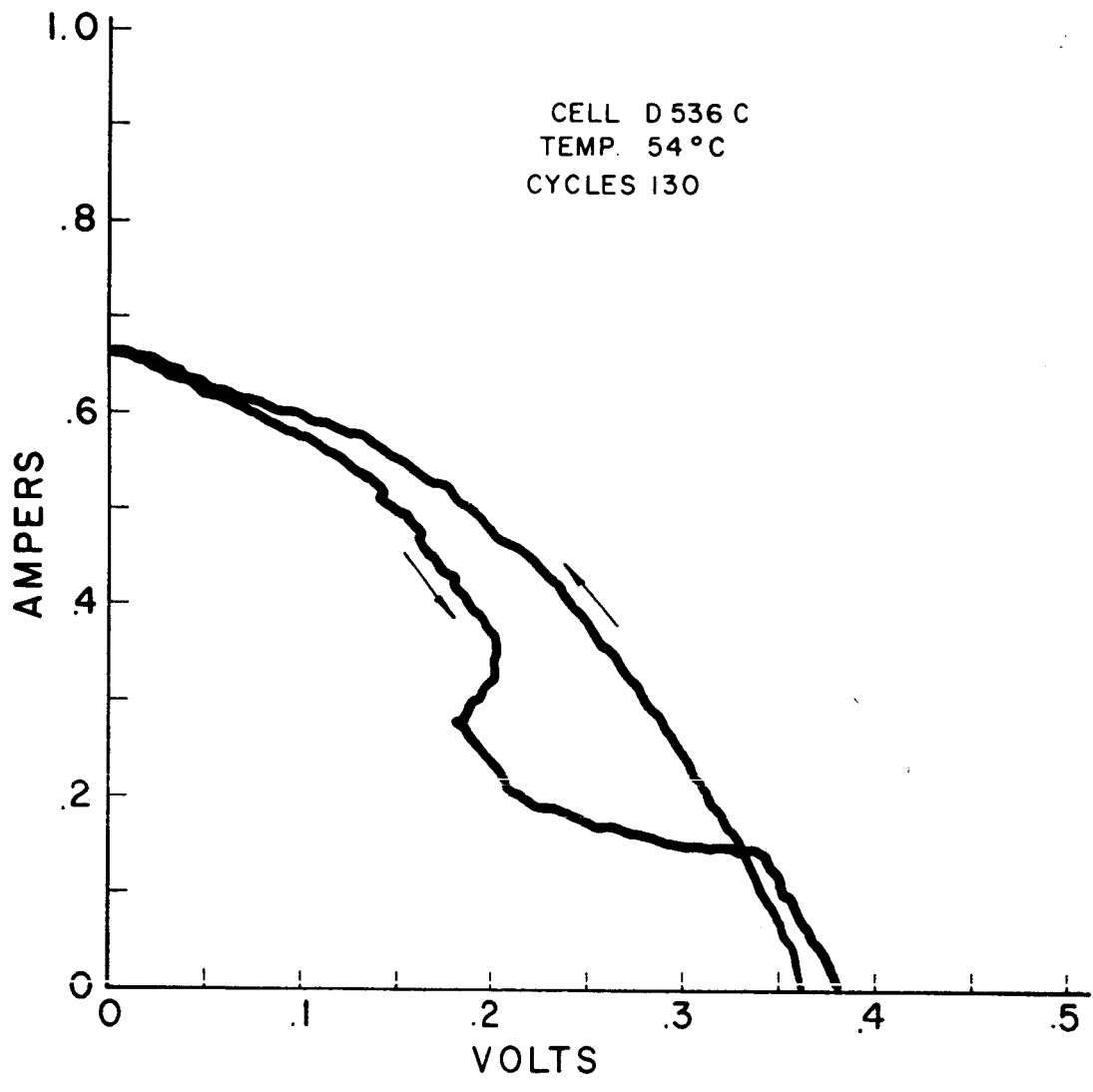


FIG. 6: ERRATIC I-V CURVE TRACES OBTAINED BY BOEING ON THERMAL CYCLING TEST.

Table XIV-A gives the initial test data for this group of cells just before shipment to Lincoln Laboratory. The room temperature fill factors for these cells were markedly better than those of the first batch sent to Boeing, but about half of these cells had only a fair shunt characteristic - i. e., the I-V curve at the short circuit condition was not quite perpendicular to the current axis.

Lincoln Laboratory forwarded these cells to Boeing where they were tested and placed on thermal cycling under approximately the same conditions as the earlier test performed for NASA. The calibration of the Boeing simulator used for these tests was subsequently found to be in error, and hence the cell outputs they obtained were at variance from those obtained at Clevite and at Lincoln Laboratory. However, the measurements taken over the course of these tests are believed to be reasonably comparable.

The cells were given a total of 77 cycles and the cells degraded steadily over that period to about 65% of their initial values. There was little or no "hysteresis" effect noticed for these cells initially, but all 9 cells showed a marked "hysteresis" as the test progressed with the effect showing up in each case at the voltage end of the curve.

The results of this test are reported in more detail in a Lincoln Laboratory Technical Note⁽⁹⁾. Table XV summarizes the average output data for the 9 cells on this test measured at Boeing after different numbers of temperature cycles. The degradation was characterized by a loss of cell efficiency primarily from a loss in fill factor, though both OCV and SCC also showed small but unmistakable drops.

After completion of thermal cycling, 5 of the cells were returned to Clevite where they were examined and retested under the standard 25°C AM1 test conditions. The data are shown in Table XIV-B, and it is seen that the cells gave nearly as much output as they had prior to thermal cycling! The slight differences were due to a drop in fill factor mostly, but also in part to a loss of short circuit current.

3. NASA Lewis Laboratory Test - October 1967 Cells

The next thermal cycling test was performed by the Chemistry and Energy Conversion Division of the Lewis Research Center, NASA, on 4 Kapton covered cells that were produced in October 1967. These cells had fill factors of 68 to 71% and AM1, 25°C efficiencies of 4.0 to 4.3%. The data are shown in Table XVI-A.

Thermal cycling was carried out with 100 mw/cm² light for a 1 hour period followed by 0.5 hour of darkness. Cell temperatures were cycled between about +41°C to -70°C. A total of 208 cycles were carried out and the cells degraded steadily, but somewhat erratically, to between about 90 to 60% of their initial values. The cells were allowed to remain under vacuum in the dark at room temperature for several days and then were retested. It was found that they had recovered to within about 5% to 15% of their initial output values. Then the thermal cycling was resumed for an additional 100 cycles. The degradation was more rapid the second time and the cells dropped to about 90 to 40% of their original values. Table XVII presents the data for selected periods of temperature cycling.

TABLE XIV

CLEVITE TEST DATA ON CELLS USED FOR BOEING
THERMAL CYCLING OF JULY 1967 PRODUCTION

<u>Cell No.</u>	<u>OCV (volts)</u>	<u>SCC (Amps)</u>	<u>Vmp (volts)</u>	<u>Imp (Amps)</u>	<u>M. P. (Watts)</u>	<u>Fill %</u>	<u>Eff. %</u>
<u>A - BEFORE THERMAL CYCLING</u>							
H110AK4	.480	.752	.380	.644	.247	68	4.5
H110AK2	.482	.725	.382	.620	.237	68	4.3
H110AK5	.475	.740	.378	.644	.244	69	4.4
H124CK5	.479	.730	.375	.620	.233	67	4.2
H106BK5	.480	.794	.368	.680	.250	66	4.6
B935AK	.470	.760	.372	.660	.245	69	4.5
H108BK8	.477	.732	.374	.635	.237	68	4.3
H99AK5	.480	.760	.373	.640	.238	65	4.3
H110AK6	.480	.750	.380	.644	.244	68	4.5
<u>B - AFTER THERMAL CYCLING</u>							
H110AK4	.487	.740	.380	.648	.246	68	4.5
H124CK5	.478	.721	.367	.632	.232	67	4.2
H106BK5	.480	.776	.368	.644	.236	63	4.3
H108BK8	.480	.702	.379	.604	.228	68	4.2
H99AK5	.479	.748	.360	.618	.222	62	4.1

Kapton Covered Cells -

Tested at 25°C in Equivalent Air Mass 1 Sunlight

TABLE XV
 BOEING THERMAL CYCLING DATA ON JULY 1967 CELLS
Average for 9 Cells

<u>Cycle</u>	<u>OCV</u>	<u>SCC</u>	<u>Vmp</u>	<u>Imp</u>	<u>M. P.</u>	<u>Fill</u>	<u>Eff.</u>
0	0.404	0.764	0.298	0.647	0.193	62.5	2.51
1	.406	.769	.295	.648	.191	61	2.48
37	.393	.742	.275	.502	.138	47	1.79
60	.386	.759	.274	.495	.135	46	1.75
77	.384	.744	.275	.457	.125	44	1.62

All cells tested in situ at approx. 60°C, 10^{-6} Torr, Air Mass 0

TABLE XVI

CLEVITE TEST DATA ON CELLS USED FOR LEWIS LAB
THERMAL CYCLING OF OCTOBER 1967 PRODUCTION

<u>Cell</u>	<u>OCV</u>	<u>SCC</u>	<u>Vmp</u>	<u>Imp</u>	<u>M. P.</u>	<u>Fill</u>	<u>Eff.</u>
<u>A - BEFORE THERMAL CYCLING</u>							
N100DK15	0.450	0.714	0.350	0.640	0.224	70	4.1
N100DK23	.480	.718	.379	.630	.235	68	4.3
N100DK7	.483	.672	.386	.595	.230	71	4.2
N100DK26	.480	.661	.377	.588	.222	70	4.0
<u>B - AFTER THERMAL CYCLING</u>							
N100DK15	.451	.720	.345	.630	.219	67	4.0
N100DK7	.490	.692	.371	.598	.219	66	4.0

Kapton Covered Cells

Tested at 25°C in Equivalent Air Mass 1 Sunlight

TABLE XVII

LEWIS LAB THERMAL CYCLING DATA ON OCTOBER 1967 CELLS

<u>Cell No.</u>	<u>Cycle</u>	<u>OCV</u>	<u>SCC</u>	<u>Vmp</u>	<u>Imp</u>	<u>M. P.</u>	<u>Fill</u>	<u>Eff.</u>
N100DK15	5	0.428	0.530	0.295	0.430	0.127	56	2.32
	164	.425	.497	.300	.390	.117	55	2.14
	308	.440	.358	.310	.310	.096	61	1.76
N100DK23	5	.448	.569	.340	.420	.143	56	2.61
	164	.425	.514	.275	.360	.099	45	1.80
	308	.422	.373	.250	.260	.065	41	1.19
N100DK7	5	.470	.512	.295	.340	.100	42	1.83
	164	.410	.480	.265	.275	.073	37	1.33
	308	.413	.344	.255	.220	.056	39	1.03
N100DK26	5	.446	.503	.321	.405	.130	58	2.38
	164	.425	.450	.288	.330	.095	50	1.74
	308	.440	.450	.315	.360	.113	57	2.07

Tested in situ at approx. +41°C, 100 mw/cm² Light Intensity

Above data are original readings uncorrected for cell temperature and light intensity fluctuations.

Two of the degraded cells were returned to Clevite and were measured under standard test conditions, and as can be seen in Table XVI-B were within 5% of the outputs that they had given originally before the test. Again, the degradation was characterized chiefly by a loss of fill factor. The OCV and SCC of these had not degraded at all.

4. M. I. T. Lincoln Laboratory Test - Oct. & Dec. 1967 Cells

The last thermal cycling test of this period was carried out at Lincoln Laboratory on groups of cells which were fabricated in October and in December of 1967. In addition to a few special experimental cells, 3 standard Mylar covered cells made in December were tested. The latter 2 cells had a narrow "U" shaped Mylar reinforcing strip cemented along each side edge of the cells in an attempt to prevent delamination at the cut edges. The Clevite test data on these cells are summarized in Table XVIII.

The cells were thermal cycled between approx. 67° to 78°C during a 1-1/2 hour hot period and -85° to -89°C during a 1-1/2 hour dark period. The conditions of the test were varied somewhat during the test due to problems with the heating and light sources, and the cells were given only 70% of the light that would be experienced in AM0 sunlight in order to keep from overheating them. A total of 81 cycles were carried out.

There was some hysteresis of the I-V characteristic curve noted for these cells initially, but toward the short circuit current end of the curve rather than at the OCV end as was experienced for the cells on the Boeing tests. The hysteresis however did not change appreciably over the period of the test. All of the cells degraded during the test, but to a lesser extent than any of the previous tests. Table XIX summarizes the data. The degradation on the Lincoln Laboratory test was calculated on the basis of the maximum power using the poorer of the two I-V curves in each case, whereas the Boeing calculations were based on the best curve when hysteresis effects occurred. Thus the Lincoln Lab degradation might have been less than indicated and the Boeing degradations might have been more than indicated. (It is not known which of the two curves would have represented the actual performance of the cells if they had been maintained with a fixed load in the vicinity of the maximum power point.)

It is to be noted that the fill factors obtained by Lincoln Lab at the cell operation temperature were approximately the same as obtained at Clevite at room temperature, whereas the values obtained by Boeing in each case were very much less. It is believed that this is due to the later vintage cells being better in this respect rather than to errors in the Boeing test circuitry.

5. Other Tests

Several other thermal cycling tests of CdS thin film solar cells have been carried out in different laboratories. In one test at Clevite a 1x2 cm size cell was mounted inside a 1" diameter clear quartz tube and an inert atmosphere kept in the tube. The leads of the cell were connected to an oscilloscope which continuously traced the I-V characteristic curve. A thermocouple mounted on the back of the cell indicated temperature. The quartz tube was alternately lowered into a dewar of liquid nitrogen and raised into the beam of a tungsten lamp. Tests of several hundred cycles on several 1x2 cm Kapton covered cells failed to show evidences of cell degradation.

TABLE XVIII

CLEVITE TEST DATA ON CELLS USED FOR LINCOLN LAB
THERMAL CYCLING OF OCTOBER-DECEMBER 1967 PRODUCTION

<u>Cell No.</u>	<u>OCV</u>	<u>SCC</u>	<u>Vmp</u>	<u>Imp</u>	<u>M. P.</u>	<u>Fill</u>	<u>Eff.</u>
<u>A - BEFORE THERMAL CYCLING</u>							
N87B1	0.479	0.980	0.370	0.860	0.318	68	5.8
N89A1	.500	.920	.390	.816	.318	69	5.8
N89A2	.492	.962	.380	.850	.323	68	5.9
H300B5*	.469	.980	.351	.858	.301	66	5.5
H302A5*	.470	1.000	.352	.870	.306	65	5.6
<u>B - AFTER THERMAL CYCLING</u>							
H302A5*	.475	.936	.360	.812	.292	66	5.3

* Mylar Reinforced Edges

Mylar Covered Cells

Tested at 25°C in Air Mass 1 Equivalent Sunlight

NOTE: Subsequent indications are that there was a calibration error for the Solar Simulator and that the initial test data (before thermal cycling) for Max. Power was approx. 8% high with both voltage and current readings involved.

TABLE XIX
 LINCOLN LAB THERMAL CYCLING DATA ON
 OCTOBER-DECEMBER 1967 CELLS

<u>Cell No.</u>	<u>Equil. Temp.</u>	<u>Fill %</u>	<u>Final Value as % of Initial Value</u>		
			<u>OCV %</u>	<u>SCC %</u>	<u>M. P. %</u>
N87B1	77°C	68	100	96	87
N89A1	76.5	69	95	100	87
N89A2	78	68	100	93	87
H300B5*	78	66	100	100	90
H302A5*	71	65	100	91	85

* Mylar Reinforced Edges

A somewhat more elaborate test was set up by the Power Systems Division of NASA Lewis Research Center which could test one cell as large as 3" x 3" at a time. Standard 3" x 3" cells did exhibit degradation on this test comparable to that obtained on the more extensive tests described in the above sections of this report. The cells that degraded exhibited delamination at the cut edges within the CdS layer. The area of the delamination in these cases approximately accounted for the loss in cell output.

On another test at the Lewis Power Systems Division setup a few cells were cut into sections in such a way as to preserve the positive and negative lead contacts. A half cell, 1-1/2" x 3" in size, exhibited less degradation than full size cells, and a quarter cell, 3/4" x 3" in size, exhibited still less degradation.

6. Analysis of Degraded Cells

Two approaches followed in trying to understand the reasons for degradation of cells during thermal cycling are the study of the electrical performance of the cells and physical "post mortems" on the cells after failure. Both approaches yield useful insights to the mechanism of the degradation.

(a) Changes in Electrical Output

Different cells have exhibited different patterns of electrical performance on thermal cycling test. In general they have been characterized by erratic electrical outputs, with the later vintage cells being less erratic and showing less degradation. Figure 7 shows the maximum power versus the number of temperature cycles for 2 cells made in 1966, tested at Boeing, and showing very severe degradation. The nearly complete sudden loss of output at one point on one cell and the nearly complete recovery a few cycles later is noteworthy. On the other cell a similar experience was recorded except that the cell stayed at nearly zero output for about 30 cycles and then recovered.

In Figure 8 is shown the change in the I-V characteristic curve of a cell that was made in April 1967 and which degraded on the Boeing test. The hysteresis effect on the initial trace appears to have been characteristic of the cells made at that time when tested at 60°C to 70°C temperature. The hysteresis was usually at the OCV end of the I-V curve and got progressively worse as the number of cycles increased. This is illustrated by the lower set of curves of Figure 8. In some cases the I-V curve itself became erratic and would not give the same curve on successive traces. The hysteresis effect at the OCV end of the curve is approximately what would occur if there was an intermittent partial short circuit which was activated at the open circuit condition and deactivated at the short circuit condition when the curve was traced. The erratic trace which would not exactly repeat itself is what might be expected from an intermittent contact in the cell. A delamination of part of the CdS away from the conductive substrate might give this effect if there were forces that held the delamination closed at times and open at other times. Of course, the erratic trace could also be the fault of the X-Y recorder or of the electronic load used to generate the curves.

In Figure 9 are illustrated the before and after I-V curves of one of the better of the latest vintage cells tested by Lincoln Laboratory. This cell degraded by 15% over 81 temperature cycles and was much less erratic in its

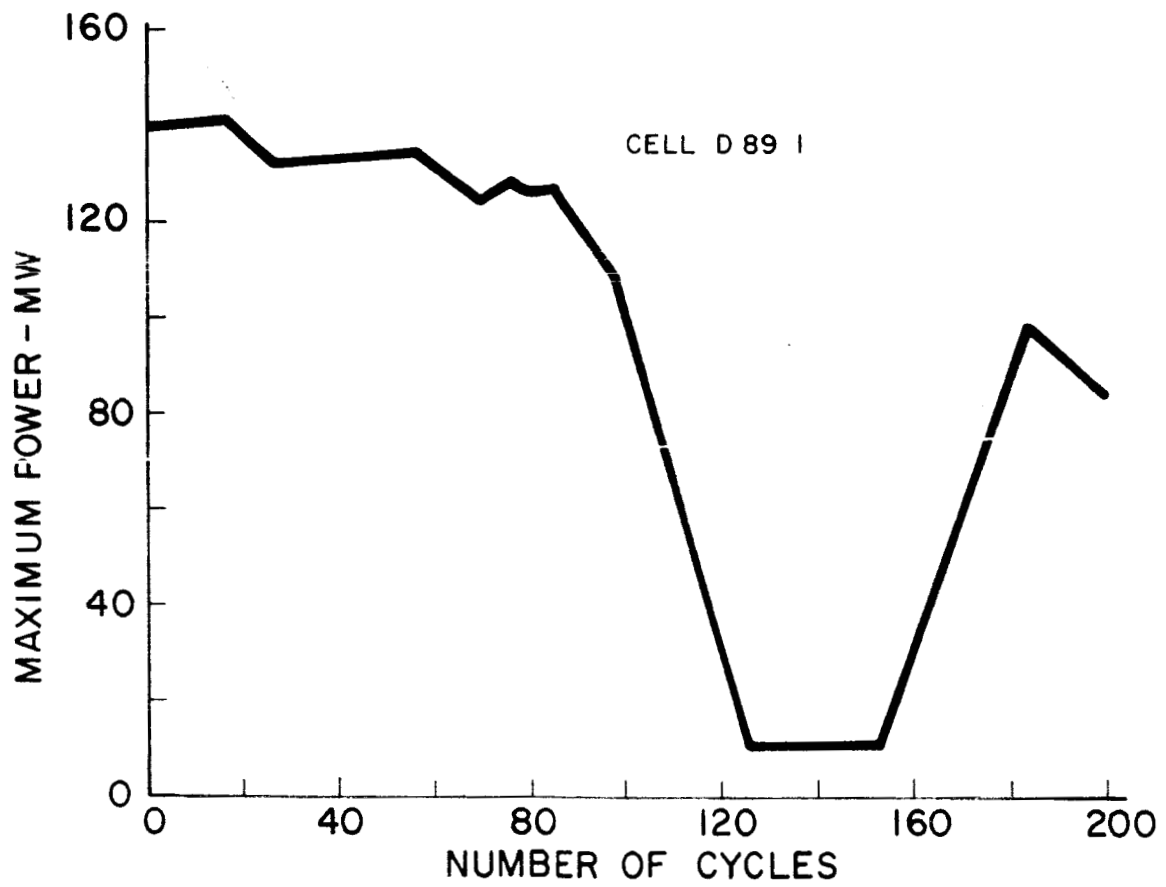
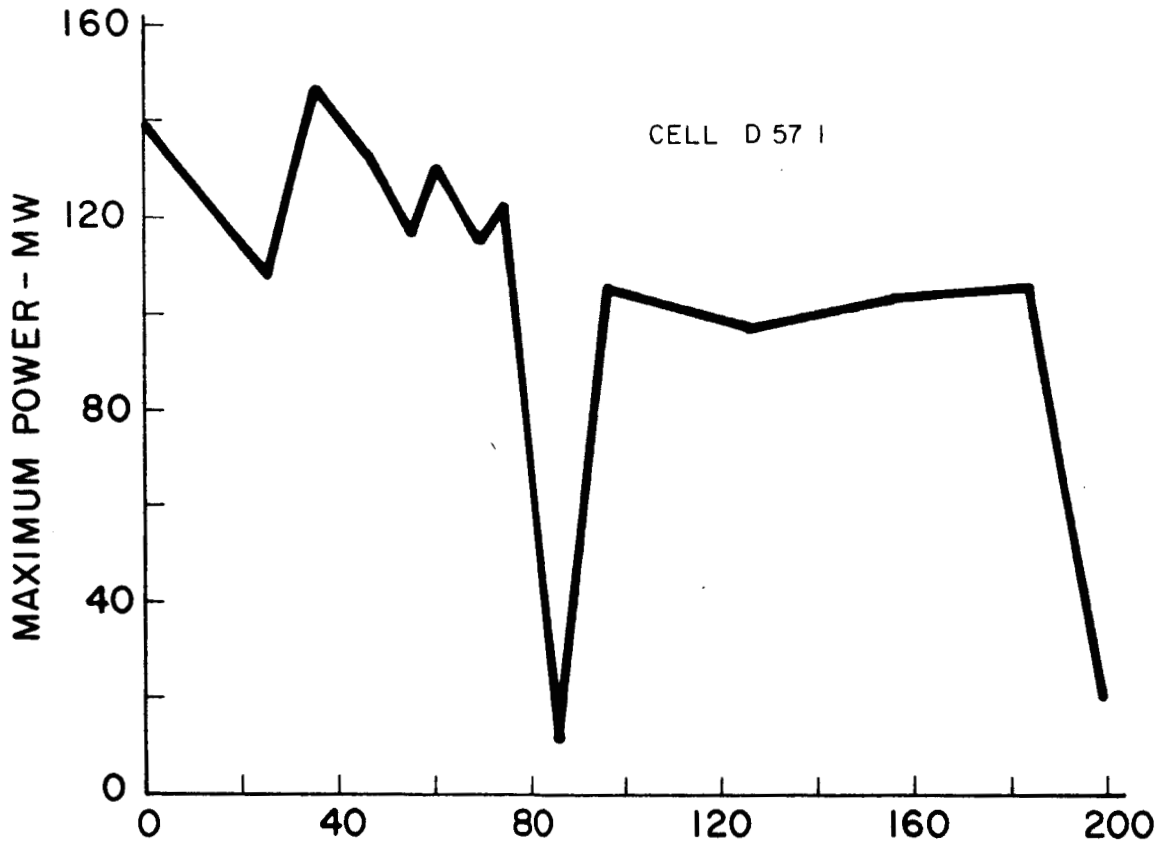


FIG. 7 : ERRATIC DEGRADATION OF MAXIMUM POWER ON THERMAL CYCLING TEST. (1966 CELLS ON BOEING TEST)

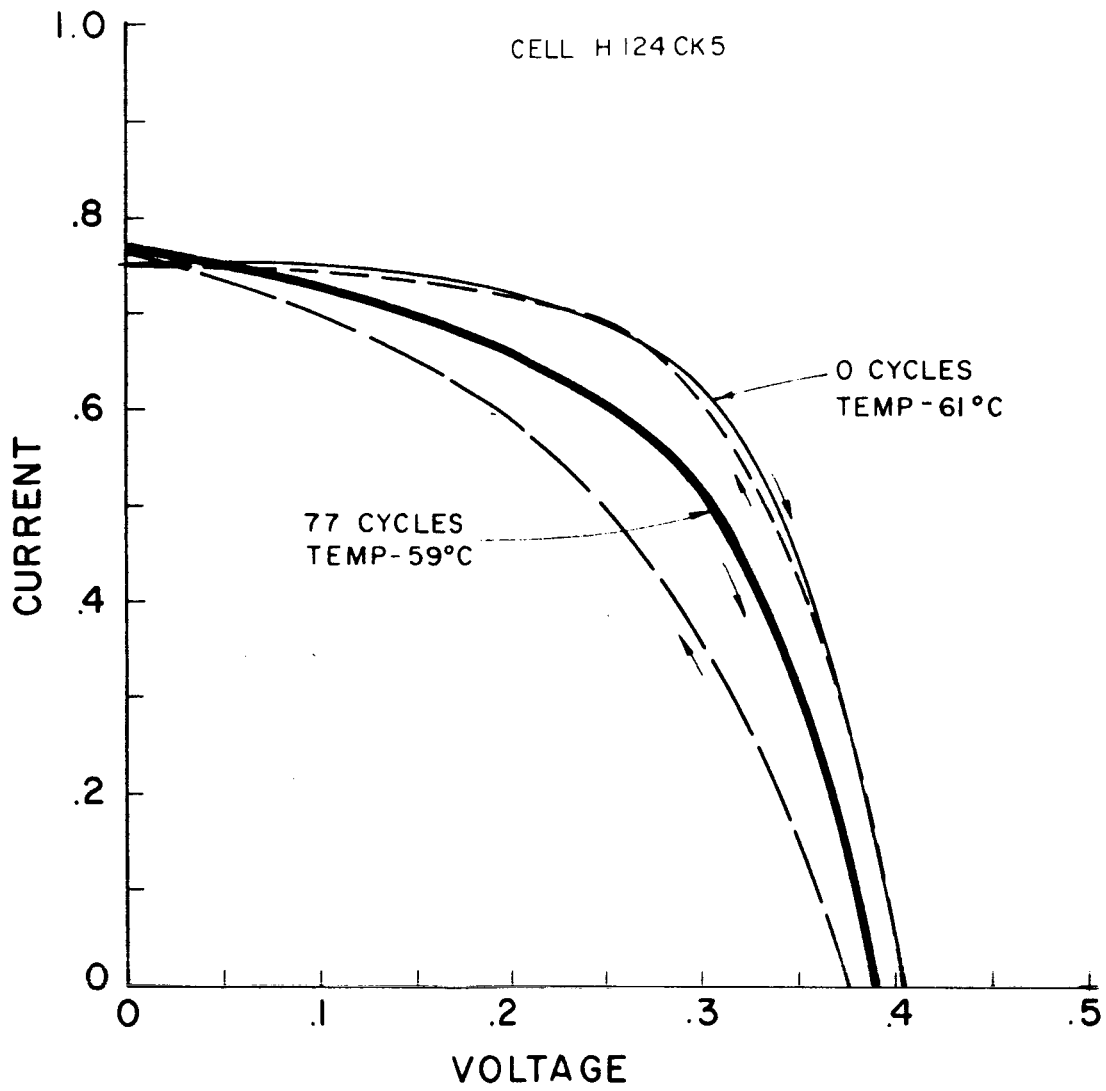


FIG. 8 : EFFECT OF THERMAL CYCLING ON I-V CHARACTERISTIC CURVE - APRIL 1967 CELL.

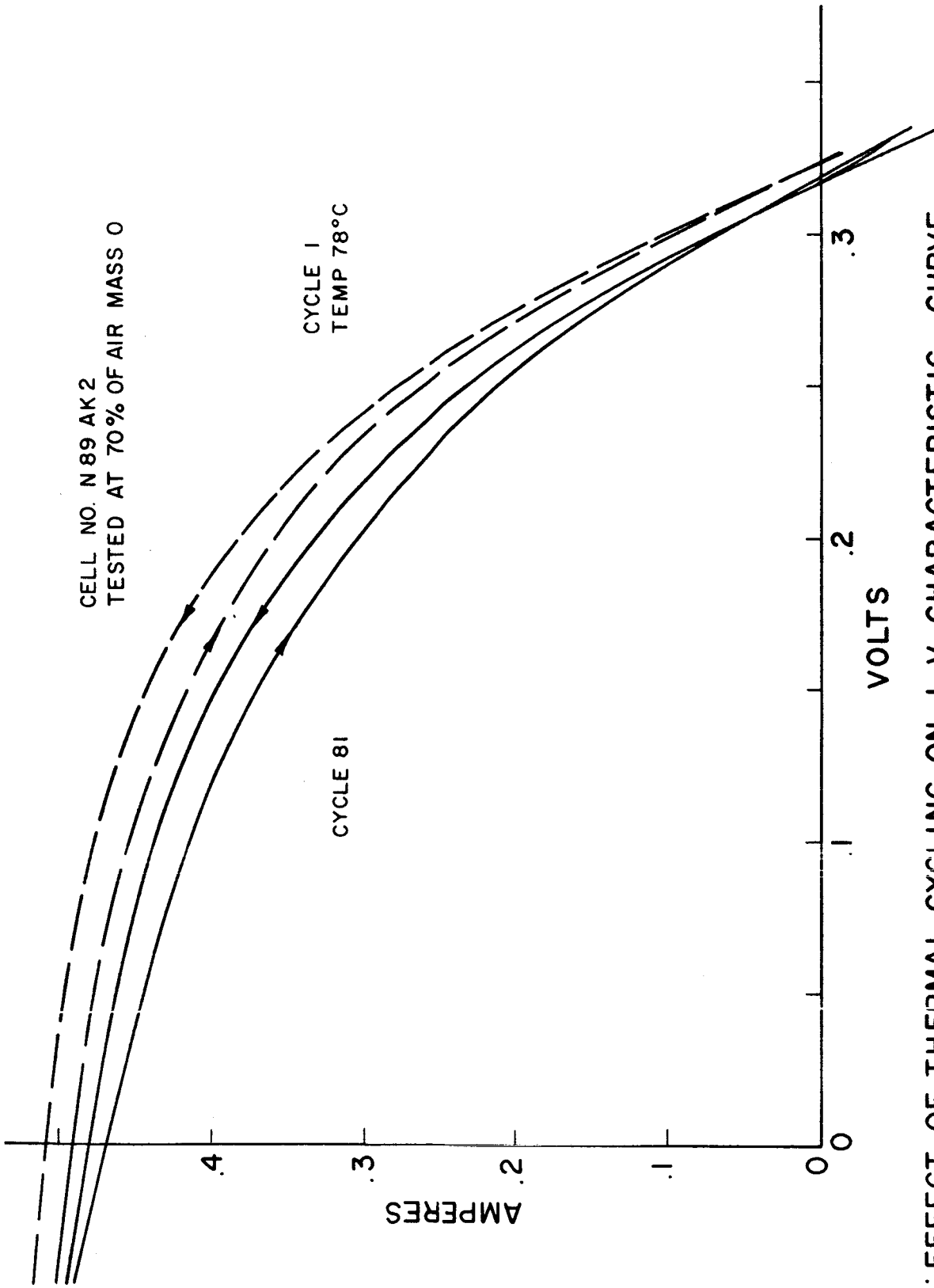


FIG. 9 : EFFECT OF THERMAL CYCLING ON I-V CHARACTERISTIC CURVE -
OCTOBER 1967 CELL. (LINCOLN LAB TEST)

behavior than earlier cells. This cell also showed a hysteresis effect, but the effect occurred at the SCC end of the curve rather than at the OCV end as was noted for the earlier cells. This pattern of hysteresis is what might occur if there were a partial delamination which was activated at the SCC condition of the cell and deactivated at the OCV condition. It is noteworthy that as this cell degraded the OCV stayed fixed and the SCC fell and the fill factor fell only slightly. It is also to be noted that the fill factor of this cell and of other cells which have performed poorly dropped considerably as the cell temperature increased - even before temperature cycling. The pattern of cell degradation which is characterized by a drop in short circuit current and a drop in the fill factor could be explained as the result of an increase in internal series resistance. In this case the fill factor changed only slightly and if the degradation were caused by an increase in series resistance a much greater change in the fill factor would be needed to account for the change in the SCC. The actual pattern observed is more likely to have been caused by a loss in active area such as would occur if a portion of the CdS film were to become detached from the conductive substrate so that the current collection from that area were greatly reduced.

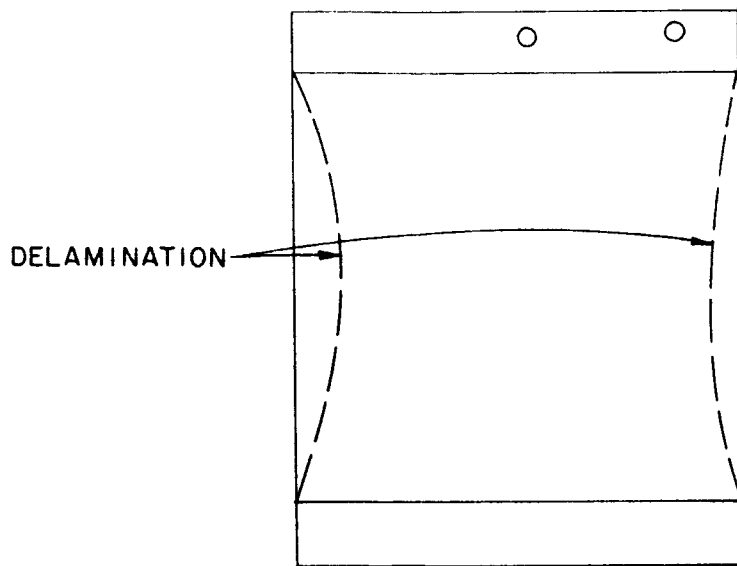
(b) Physical Changes

Some of the cells that were degraded on thermal cycling were returned to Clevite for testing and examination. Electrical tests on the degraded cells were relatively uninformative as much of the degradation reported could only be observed by in situ measurements during the actual thermal cycle test. (The electrical changes discussed in paragraph 6a above were in situ measurements supplied by the testing agency in each case.) The physical examination of the cells was more informative.

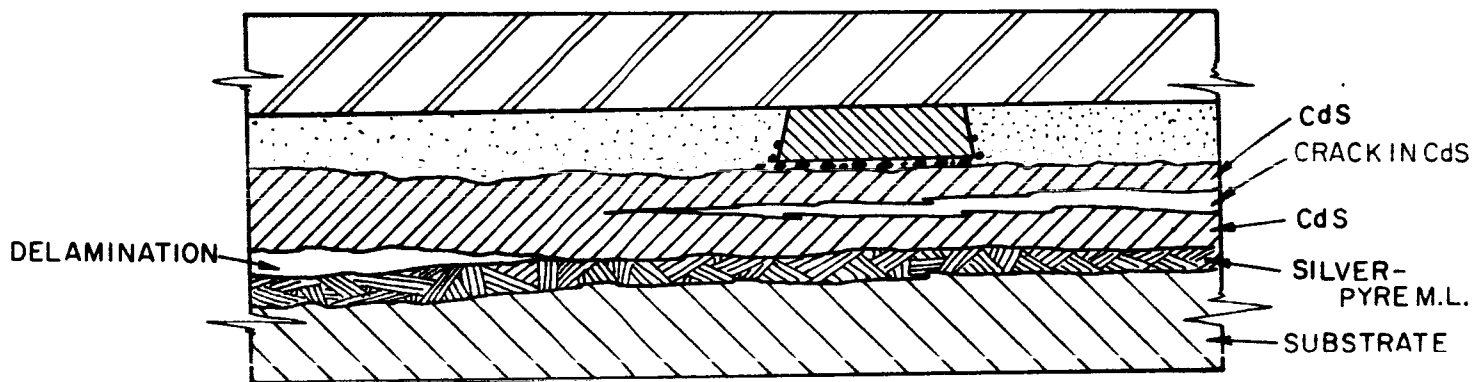
Several of the most severely degraded cells were characterized by a delamination of the CdS film from the conductive substrate at the edges of the cell. This is illustrated in Figure 10-A. In those cases, the actual area of the delamination accounted for most of the permanent loss (i. e., that which was not recovered after the cells were removed from the test) of output. For example, Cell D536A when returned from the Boeing test showed permanent degradation of output of 15% (under Air Mass 1, 25°C test) characterized by a reduction in SCC. This cell had delaminated at the edges and the measured area of that delamination was approx. 15% of the cell area.

A number of cells, some that had not been thermal cycled and some that had been thermal cycled, were carefully potted, cross-sectioned and polished and studied under the microscope. Such photomicrographs of cross-section views of CdS cells have been helpful in the past in the study of the grid contact, and of the structure of the CdS film. In this instance, the studies disclosed a number of lateral cracks in the CdS films, and delaminated areas between the CdS and the silver Pyre-ML conductive substrate coating. These cracks and delaminations appeared to be much more prevalent in the cells which had been degraded on thermal cycling than they were on fresh cells. These cracks and delaminations are sketched in Figure 10-B.

The cracks appeared to be stress-induced and in some cases seemed to have been transmitted to the CdS film by a grid wire, as there was some evidence of iteration of the crack pattern corresponding to the grid wire spacing. In a number of cases the depth of the lateral cracks appeared to be about 5 microns and to correlate with the maximum penetration of the Cu_2S along grain boundaries.



(a: DELAMINATION OF A THERMAL CYCLED CELL



(b: LATERAL CRACK IN CdS AND DELAMINATION AFTER THERMAL CYCLING.

FIG. 10: LATERAL CRACKS AND DELAMINATIONS OBSERVED AFTER THERMAL CYCLING.

Also, in some cases the cracks appeared to initiate at the substrate at the site of a delamination of the CdS from the substrate.

These lateral cracks and delaminations have been noted independently at both Clevite and Lincoln Laboratory, though the extent and probable significance of the cracks were recognized first at the latter.

In some cases it has been possible to start a lateral crack in the CdS layer at a corner of the cell and to cause the crack - via peeling forces - to propagate across the entire 3" square area of the cell so that the barrier layer and part of the CdS layer remain intact attached to the grid and cover plastic while the bulk of the CdS film remains attached to the substrate.

Other nonhomogeneities in the CdS cells after thermal cycling were disclosed by infrared thermograms which were taken at the Barnes Engineering Company by Lincoln Laboratory personnel. These were taken by running a current of 1 ampere in the forward direction through a freely suspended cell and scanning the cell with an infrared sensor to measure the pattern of temperature rise caused by the current flow. Photographic reproductions of such I-R thermograms were shown in reference 9.

Fresh untested cells generally showed a relatively uniform temperature within a few degrees across the entire surface of the cell. However, some cells showed hot spots and cold spots indicative of nonhomogeneities in the conducting path. In one case a cold spot could be correlated with a poor grid contact due to missing conductive epoxy cement over a portion of the grid. In other cases, hot spots suggested localized shorting paths through the CdS film. Temperature rises were frequently of the order of 30°C and in one case a differential of 135°C was observed.

A number of additional infrared thermograms are being taken on a group of cells prior to temperature cycling and these will be compared with others to be taken after thermal cycling.

(c) Interpretation of Results

Widely different performance patterns have been observed for different CdS thin film solar cells in the various thermal cycling tests described above. Variations in the thermal cycling test conditions themselves may account for some of these differences, and interpretation of the data is undoubtedly complicated by some inaccuracies in measuring cell outputs. However, there seems little doubt that most of the differences are due to variations in cell quality. It is evident that the cells fabricated in the last year are not stable on temperature cycling.

The instabilities observed in recent vintage cells have frequently been intermittent in nature and cannot generally be characterized by a systematic change of cell properties. This makes it unlikely that degradation is due to an intrinsic change in the cell - i. e., in the barrier layer, in the insulating layer, or in the CdS semiconductor. Rather, the degradation appears to be mechanical in nature. A number of different observations all lead to this conclusion.

There have been many nonhomogeneities observed in cells of the present vintage. Major differences in the continuity of the silver Pyre-ML coating are readily seen by examining the substrates in front of a strong light. Such differences could cause hot and cold spots in the cells under full electrical load and these in turn could create high localized stress concentrations which could lead to cracks and delaminations. The condition of course could get worse as it progressed. Wide differences in the physical integrity of the CdS film itself, of the adhesion of the CdS film to the substrate and of the distribution and continuity of the conductive gold epoxy cement have been observed on regular production cells. All of these could lead to uneven stress distributions and eventual failures. Until the middle of 1967 the control of quality of the fabrication process was entirely a matter of individual operator attention. Gradually in this period, more detailed specifications for component parts, materials and process parameters and for in-process cell quality have evolved and procedures for inspection and quality assurance have been instituted. The quality control program is believed responsible for the improvement in cell stability which has been observed during the last year, but it should be realized that this program is still far from adequate.

While corroborative data are being sought in experiments planned for the next few months, there does appear to be a very high probability that the cracks, delaminations, flaws and various nonhomogeneities in cell construction account for the major portion of cell degradation on thermal cycling. It seems probable that the forces exerted by the differential thermal expansion between the various material layers which comprise the CdS thin film cell act on the flaws and discontinuities to cause cracks, delaminations, etc.

It seems probable that excessive compressive and tensile forces are being used in processing the cells during the cell gridding and cover plastic lamination steps. The apparent ruggedness of the CdS cell may have allowed overly abusive handling and processing practices to become established. These factors may predispose the cells to failure under extreme environmental conditions. In any case, many of these factors can be controlled and steps are being taken to do so. Also, there are some design changes which can be made which may help to alleviate the buildup of stresses in the cell package and others which may help to better contain those stresses. Included among the changes being evaluated are a zigzag or a wavy grid pattern that could "give" on thermal contraction, and flexible epoxy cements that should not transmit as much stress from the grid or cover plastic to the CdS layer. Carrying the cover plastic further up onto the lead tabs and using a reinforcing bead along the cut edges may keep stress concentrations from starting delaminations.

IV. CELL DESIGN IMPROVEMENTS

A. Semiconductor - Substrate Interlayer

If the CdS is deposited directly on the silver Pyre-ML substrate, a rectifying contact results and cell outputs are very low indeed. Zinc is used to provide an ohmic contact between the silver Pyre-ML substrate and the CdS film. Zinc forms an excellent low resistance ohmic contact, and the zinc is readily deposited from conventional electroplating baths.

The chief disadvantage of zinc has been its relatively high vapor pressure at the temperature at which the substrate is maintained during CdS evaporation. There is some tendency for zinc to evaporate off of the substrate prior to the start of evaporation and then to re-evaporate from the adjacent tooling later in the evaporation cycle when the whole system warms up. While it has been difficult to prove the point, it has been suspected that such zinc re-evaporation has caused excess amounts of zinc to be included in the CdS film with a consequent loss in the semiconducting properties of the CdS and a lowering of CdS cell output.

Further, it has been suspected that later on the zinc may diffuse into the CdS, and possibly also into the silver of the silver Pyre-ML layer, when the cell is fabricated and subjected to high temperature storage conditions. Bearing out this suspicion it has been noted that some cells show an unusual degree of discoloration when viewed through the Kapton substrate after 150°C vacuum storage for about 4 weeks. This discoloration is a mottled sort of blackening and is frequently accompanied by a loss of adhesion of the CdS to the substrate. For these reasons a number of alternative materials have been evaluated as possible substitutes for the zinc interlayer.

1. Chromium

Evaporated chromium layers were evaluated a year ago using both an ordinary grade of chromium and a special high purity grade⁽³⁾. In both cases excellent ohmic contacts resulted, and the I-V characteristic curves of the cells fabricated with the chromium were very rectangular. However, the cells gave relatively low short circuit currents and low efficiencies - about 25 to 30% below what was obtained from zinc interlayer cells.

Additional experiments with chromium interlayers were tried in this period. With the thought that Chromium might be contaminating the evaporator and thus poisoning the subsequently evaporated CdS film, a group of cells were fabricated using separate evaporations for the chromium under coating and for the CdS film itself. After the chromium was deposited onto the silver Pyre-ML substrates, they were removed from the evaporator, the evaporator was thoroughly cleaned, and then the substrates were put back into the evaporator for the CdS film deposition.

The chromium interlayer cells still gave very low outputs - less than half that of control cells with zinc interlayers. All of the more recent cells with chromium had I-V curves with double inflection points, as if there were two back-to-back junctions. This is in direct contrast to earlier tests of chromium interlayers where excellent rectangular I-V curves were obtained. This may be a result of removing the chromium deposits from the evaporator where they could oxidize prior to CdS film deposition.

2. Aluminum

Aluminum is an attractive possibility as an interlayer material between the silver Pyre-ML substrate and the CdS film as it also makes an excellent low resistance contact to CdS. It is a good electrical conductor and has a low vapor pressure. There is every reason to believe that aluminum would not tend to diffuse away into either the CdS layer or into the silver substrate. The chief drawbacks of aluminum are its tendency to form an insulating oxide layer and the possibility of a highly water soluble sulfide being formed which could result in a moisture sensitive cell.

The possibility of a water soluble aluminum sulfide layer causing difficulty should be minimal if the layer were completely covered with an impermeable CdS layer - which should always be the case. In order to overcome the problem of oxide formation, a process was developed whereby the aluminum evaporation was gradually phased out as the subsequent CdS evaporation was phased in. Thus, the vacuum was never broken between the two layers and there was no distinct interface between them.

Well adhering CdS films were obtained by these techniques, and a few reasonably efficiency cells were fabricated from them. The highest output cell was 5.3% efficient. However, most of the aluminum interlayer cells were between 4 and 5% efficient, or about 20% less than the standard zinc interlayer cells processed over the same period. Table XX gives the data for the better aluminum interlayer cells processed in this period.

It is not clear why the aluminum interlayer cells have not given as much output as the zinc interlayer cells. It is possible that the zinc presents a different surface for the nucleation of the CdS which in some way is more favorable for the structure of the CdS film and also for the formation of the Cu_2S barrier layer. However, our ability to characterize the structure of the CdS film is very limited, and this remains another poorly understood portion of the technology of CdS solar cell fabrication.

It is of interest that several of the aluminum interlayer cells have given the best stability results on the 150°C vacuum storage test. However, this may be a statistical accident since only a few of these cells have been put on that test.

B. Copper Substrate

Some of the highest efficiency CdS thin film solar cells have been formed using CdS films that were deposited on copper foil substrates in place of the Kapton plastic substrates. The reason for the higher efficiencies appears to have been chiefly due to the higher conductivity of the 0.001" thick copper substrate which minimized series resistance effects from the substrate. Though the copper foil substrate is probably more economical than the plastic substrate, the difference is not great and there would be little advantage to the copper substrate unless it did yield higher conversion efficiencies than could be obtained from the plastic substrate cell.

On that possibility the copper substrate cells were extensively evaluated in this period. However, considerable difficulty with good CdS film adhesion to the substrate was encountered, and most of the effort was placed on trying to improve the adhesion. These results were only partially successful and because of better results being obtained from the silver Pyre-ML coated plastic substrate cell, the work with the copper substrate cell was finally discontinued.

C. Evaporated Grid Contact

Earlier⁽¹⁰⁾ a technique was developed of depositing a gold grid on the barrier layer by vacuum evaporation using a mask of a fluorocarbon release agent. The fluorocarbon was sprayed onto the cell barrier from an aerosol can with a standard etched (or electroformed) grid placed in front of the barrier as a mask. If the spraying were done gently the fluorocarbon would not work under the grid nor lift it off, and a clean pattern resulted.

TABLE XX
PERFORMANCE DATA OF ALUMINUM INTERLAYER CELLS

<u>Cell No.</u>	<u>OCV</u>	<u>SCC</u>	<u>Vmp</u>	<u>Imp</u>	<u>M. P.</u>	<u>Fill</u>	<u>Eff.</u>
A977A	0.465	0.735	.370	.605	.224	64	4.0
A977B	.464	.695	.366	.600	.219	68	4.0
A977D	.452	.734	.344	.577	.197	59	3.6
A981C	.471	.820	.363	.690	.251	64	4.5
A981D	.470	.800	.350	.690	.242	65	4.5
A995C	.472	.724	.369	.640	.236	67	4.2
A997A	.480	.772	.364	.690	.251	68	4.6
A997B	.483	.800	.390	.685	.267	70	4.9
A997D	.482	.800	.386	.670	.259	67	4.7

All Cells with Mylar Cover Plastic
Tested at 25°C in Simulated AM1 Sunlight

When this barriered cell was placed in the vacuum chamber and metallic gold was deposited by thermal evaporation, the gold would not adhere to the area where there was fluorocarbon, but would to those areas where there wasn't. It was necessary to find the right parameters for the gold deposition - but this was not too difficult. (The source to substrate distance had to be large enough to keep from overheating the substrate, and the gold evaporation rate had to be kept low or the gold would stick to the fluorocarbon coated areas.) After evaporation of the gold grid the fluorocarbon was readily removed in a solvent rinse without damage to the gold grid or to the cell barrier.

The difficulty with these evaporated gold grids was that they were too thin to carry the high currents generated by the high efficiency CdS solar cell, and a very high series resistance resulted which kept cell efficiencies very low. If the thickness of the gold were increased much beyond about a micron, poor adherence of the gold grid was experienced.

However, the evaporated gold contact to the Cu_2S barrier could be very advantageous because of the very intimate low resistance ohmic contact which it makes and because it is very adherent. In an effort to combine the potential advantages of the evaporated grid with the current carrying capacity of the metal mesh grid, both types were employed at the same time. Gold grids were evaporated onto standard 3" x 3" cell barriers to a thickness of about a micron. Then a standard gold plated copper metal mesh was attached with the standard gold filled epoxy cement over the evaporated grid. An attempt was made to register the cemented grid over the evaporated grid, but this was only partially successful. It is estimated that the combination grids resulted in an addition of about 10% of the active cell area being lost due to the opaqueness of the extra evaporated gold grid.

Table XXI summarizes the output of 4 cells that were made in this fashion. The outputs were slightly low, mostly probably because of the loss of active area. However, good OCV's and fill factors were obtained. These cells were sent to NASA for evaluation on temperature cycling test, since one of the suspected weaknesses of the present design cell was the permanency of the cemented grid contact. Initial indications from NASA are that these cells are holding up well, but not very many cycles have been accumulated as of this writing.

TABLE XXI

PERFORMANCE OF CELLS WITH EVAPORATED GOLD GRIDS
AND OVERLAID STANDARD CEMENTED METAL MESH GRIDS

<u>Cell No.</u>	<u>OCV</u>	<u>SCC</u>	<u>Vmp</u>	<u>Imp</u>	<u>M. P.</u>	<u>Fill</u>	<u>Eff.</u>
N108A2	.480	.742	.389	.650	.253	71	4.6
N108A5	.474	.778	.369	.685	.252	68	4.6
N108C6	.490	.720	.390	.605	.235	67	4.3
N108C8	.480	.661	.380	.580	.220	69	4.0

All cells with Mylar cover plastic.
Tested at 25°C in Simulated AM1 Sunlight.

D. Alternate Grid Designs

A number of alternate types and designs of grids have been tried in this period in hopes of achieving a more economical gridding method, or of achieving a more stable cell on thermal cycling. Most of these experiments were inconclusive and additional data are needed.

A small quantity of 40 line per inch and 30 line per inch metal mesh grids of the same type presently being used with a 60 line per inch spacing were obtained from the vendor and tried on cells. The coarser spacing grids if successful could be manufactured by much more economical methods than the photo-etching process presently being used. While there were not sufficient cells run in this period for a conclusive answer to be obtained, it did appear that lower outputs were the result of the coarser grid spacing, and it was the series resistance of the cells that was affected.

A few cells were processed with electroformed solid gold grids in place of the usual gold plated etched copper grids. This was done to cover the possibility that some factor such as the hardness of the copper grid or the presence of impurities in the standard grid might be degrading cell output. A few of these cells gave appreciably higher outputs initially than the standard gridded cells. This was subsequently attributed to a combination of higher light transmission through the electroformed grid and a calibration error in the test equipment. These cells did not give as good a result on thermal cycling as the standard gridded cells, though only a few were tested.

A few cells were fabricated with a special grid design that was chosen so that any stresses on the grid would be alleviated by a slight distortion of grid geometry. This also was for the purposes of stability on thermal cycling. The results of this experiment were inconclusive.

In another experiment, the standard gold plated copper grids were annealed to a dead soft temper and used in cells. Again the idea was to prevent stress concentrations being transmitted via the grid wires. None of these cells was temperature cycled; however, a few were put on the 150°C vacuum test and these were no better than the standard cells on this test.

In another experiment, thicker grids were obtained and evaluated. These were 1 mil thick in place of the usual 0.45 mil thick grids. The idea was that the thicker grids might be more economical and that they would have greater current carrying capability. The thicker grids can be used, but there are some problems such as an extra amount of epoxy cement required for cover plastic attachment to fill in the larger space between the cell and the cover plastic. More work is needed on these before it can be determined if there is any advantage to using a thicker grid.

Further work with alternate grid designs is still desirable but it seems increasingly evident that this is a matter of economics rather than of cell stability.

E. Alternate Cover Plastics

One of the difficulties with the present method of cover plastic attachment is that the pressure used to laminate the plastic to the cell may cause the epoxy

cement to work in under the grid wire and force it away from the barrier, thus causing partial loss of the grid contact. One way to avoid this is to apply the cover plastic by casting it in place. Mylar and Kapton are understood to be cast films and hence would be amenable to this method of application.

In order to determine if this approach might be practical, the use of clear epoxy was tried as a cover plastic. A low temperature curing epoxy was used. It was applied by spreading it across the surface of a cell with a cemented grid in place and then letting the epoxy cure in a low temperature vacuum oven with no pressure applied. No significant change in the outputs of the cells was noted as a result of this method of cover plastic application. Cells gave the same output after curing of the spread-on epoxy as they had given prior to its application.

Six cells were packaged in an experimental cover plastic which was represented by the manufacturer as having the high temperature properties of the standard polyimide film and some resistance to radiation (cobalt 60) but without the amber color of Kapton. These cells gave reasonable conversion efficiencies, with a maximum of 5.0% being obtained. These cells are undergoing various tests, and some of the plastic films are being tested at NASA, Lewis Research Center for their resistance to particle radiation and to UV.

Earlier in the Contract, an attempt was made to use Pyre-ML as an 0.2 mil thick overspray onto the surface of Mylar packaged cells. The Pyre-ML overspray was dried to a tack-free condition, but was not cured. The thought was that in this condition the dried Pyre-ML would still be water white in color and hence not reduce the transmission of light to the cell, yet would act as a protective layer as far as UV and particle radiation were concerned. The tests for these latter factors were never completed however. The supplier of the Pyre-ML varnish advised that it would be expected to cure gradually in space and eventually take on the properties of Kapton, including Kapton's amber color.

V. FABRICATION PROCESS IMPROVEMENT

A. Substrate Preparation Process

Several alternate methods have been considered and evaluated for providing the conductive layer on the Kapton substrate. This conductive layer is the negative current collecting electrode of the cell. Among the alternate methods are: an aluminum foil laminated to the Kapton with epoxy cement, a commercially available copper clad Kapton film, commercial vacuum evaporated coatings on Kapton, and electrolessly plated Kapton films. The evaporated coatings were all too high in electrical resistance to be satisfactory CdS cell substrates - coatings of 0.25 ohms per square were the best that could be obtained. The commercial copper clad Kapton could not be obtained without a high incidence of pinholes in the copper. The laminated aluminum foil and electroless deposited copper and silver films produced cells with substantially lower cell outputs than the standard silver Pyre-ML process.

It is possible that more work with some of these alternate methods, and particularly the latter two, would produce satisfactory results. However, when the silver Pyre-ML coating is properly done, it makes a very good substrate. Therefore, the bulk of the effort has gone into improving the standard process.

A mixture of 1 part silver flake pigment to 2 parts Pyre-ML binder, solids by weight, has been standard for some time for this application. Since this represents only about 10% silver by volume in the finished coating, and since this coating requires burnishing prior to zinc plating, attempts have been made to increase the pigment-to-binder ratio. In every case, substantially poorer adhesion of the conductive layer to the Kapton resulted when the pigment-to-binder ratio was increased to about 2:3 or more. There appears to be an incompatibility problem when more silver is added to the Pyre-ML varnish. This has been verified by the manufacturer of the Pyre-ML, though we do not understand why this should be so.

The standard 1:2 pigment-to-binder ratio has produced conductive substrates with sheet resistances on the order of 0.01 ohms per square for thicknesses of 0.25 to 0.30 mils. This was adequate to produce 3" x 3" size Mylar covered cells with conversion efficiencies (AM1 @ 25°C) between 4 and 6%. It was noted that the higher efficiency cells were those with higher short circuit currents of about 1.0 to 1.1 amperes. However, these higher output cells also had lower fill factors of about 65 to 67%, whereas the lower output cells had fill factors up to 70%. It was then realized that it was series resistance that was limiting the output of the better cells and that this was due to the conductive substrate layer.

In an attempt to improve the conductivity of the substrate, therefore, experiments were run with thicker silver Pyre-ML layers. As the thickness was increased from 0.25 to 1.0 mils, in steps, the sheet resistance as measured with a 4 point probe did indeed decrease, but far short of the expected amount. Even more surprising, however, was the fact that the conversion efficiencies of cells made from these thicker, more conductive substrate layers decreased rather than increased.

It appears that there was an increased tendency for the silver flake pigment to segregate to the bottom of the Pyre-ML binder as the binder cured, leaving relatively few silver flakes "floating" on the surface. The increased binder layer thickness must have made worse the nonhomogeneities which were already at an intolerable level. Therefore, subsequent effort in this area was placed on improving the standard process to yield a more homogeneous silver Pyre-ML coating.

Photomicrographs of cross-sectioned standard silver Pyre-ML coatings disclosed some laminar concentrations of silver flakes and other regions that appeared to be devoid of silver particles. The differences were delineated markedly by differences in the optical density of the coated substrate (when placed over a strong light in a darkened room).

Much of the unevenness in distribution of the silver pigment appeared to be due to uneven application of the thinned silver Pyre-ML mixture in the first place. More attention was placed on the paint spray equipment used to apply the mixture, on the evenness of the spray pattern, and on obtaining a uniform motion of the spray pattern across the substrate surface. In the last month this approach has appeared to be successful in eliminating the gross nonhomogeneities that were obtained earlier. The average sheet resistance of the conductive coating has been decreased to about 0.006 ohms per square for the same thickness and composition. This, in combination with more rigorous visual inspection of the substrates, has resulted in greater uniformity and higher cell outputs and fill factors. Further improvements in this process can probably be achieved and more work in the area is planned.

B. CdS Film Evaporation

When additional fabrication facilities were added early in this period, major difficulties were encountered with the new larger vacuum evaporation equipment. The greater number of films evaporated at one time required some changes in the tooling. The larger system generated considerably more heat and the metal vacuum chamber in place of the earlier glass chamber caused a different temperature distribution pattern of the system. In addition to the usual problems of control of the evaporation parameters there was a problem of uniformity over the larger area being processed. The I-V characteristics of the cells finished from the films processed in the larger evaporator were markedly different, with slightly higher open circuit voltages and slightly lower short circuit currents than had been obtained with the smaller evaporator. Our ability to characterize the CdS films has always been very limited, and in any case there were more pressing problems.

The main problem with CdS films has been pinholes in the films, and in essence this problem has been with us from the very beginning of the CdS thin film solar cell project. Pinholes cause difficulty as they can be the site for a direct short circuit of a finished cell if the conductive epoxy works into the pinholes, or if the Cu_2S layer forms down the sides of the pinhole to make direct contact with the conductive substrate layer. In the latter instance the short circuit path may have enough resistance so that the cell output is only partially affected. Also, if the zinc on the substrate shows through a pinhole and is contacted by the CuCl barrier forming solution, elemental copper is precipitated from the solution which has a severely detrimental effect on the Cu_2S layer.

For some reason, the new large evaporator caused a great deal of difficulty with pinholes, and it was many months before this factor was brought under a reasonable degree of control. Pinholes may be caused by a nonhomogeneity or spot of contamination on the surface of the substrate, and hence the uniformity of the silver Pyre-ML layer and the evenness and cleanliness of the zinc plating on the silver Pyre-ML layer are very important. Even more important, however, is the control of spattering of solid powder particles of CdS from the sources to the substrate. This spattering results, of course, from the too rapid transfer of heat to the CdS charge. Since CdS does not go through a melting stage in this process, the edge of the charge can overheat causing its decomposition with such violence that some particles are blown out of the source. These can and do travel to the substrate in some cases and stick there. However, these solid particles may become dislodged later leaving a pinhole. Even if they do not become dislodged in subsequent processing, they are not properly incorporated into the structure of the growing CdS film and do cause a nonhomogeneity or flaw which can be the site of a later instability.

There have been a number of special evaporation sources designed to cope with the problem of spattering of non-melting materials. However, those that have been tried here have all had the disadvantage of holding too limited a size charge, or having too slow an evaporation rate, or they were of such design that adequate control of evaporation rate was not practical. A partial solution to the problem has been reached in this laboratory by using a plug of quartz wool in the neck of each evaporation source, reducing slightly the rate of CdS evaporation, and depending on a detailed 100% visual inspection under the microscope to reject from further processing those films containing pinholes.

C. Grid Contact

The process for establishing contact between the metal mesh grid and the barrier layer using conductive gold epoxy cement was developed because of the earlier experience with intermittent grid contacts when the cover plastic held the grid in place. When clear epoxy cement was substituted for the Capran adhesive for cover plastic attachment, that problem may have become less critical. However, in view of the requirement for long term stability under the rigorous conditions of space, it was believed safer to provide a permanent positive contact. Thus the gold epoxy cement process was adopted.

However, the technology for establishing such a positive and permanent contact had to be acquired by experience. Photomicrographs of cell cross-sections have frequently disclosed substantial areas where there was no gold epoxy cement under grid wires. There have appeared to be two ways in which this condition can happen. One is that the grid is not completely coated with gold epoxy cement in the first place. Control of this factor has been greatly improved by better training and supervision of the operators applying the epoxy cement to the grids, and by establishing a 100% inspection of the coated grids before they are used in the cells.

In order to facilitate the 100% inspection step, a small amount of fluorescent dye has been tried in the gold epoxy cement with the grids being inspected in a dark room under ultraviolet light. This does appear to ensure better control of the grid coating process. Preliminary indications are that the cell output is not affected by the dye. A more extended trial of this dye will be carried out before it is standardized into the process however.

The second way that the cement can be missing from part of the grid is for the grid to be put down on the cell and then shifted to another position so that some of the cement is left behind. Cleanliness of the grid itself helps in this respect. More important is the skill of the operators who assemble the cells in positioning the grid on the cell so that it is correctly placed the first time and does not need to be shifted. Better jiggling may help here. Another possibility is to use an epoxy cement which dries tack-free and hence would not track if shifted on the cell prior to curing of the epoxy. So far, however, a suitable epoxy with this tack-free drying capability has not been located.

An even more important factor governing the reliability of the gold epoxy grid contact is the proper curing of the epoxy. As with all epoxy cements, certain procedures are necessary to ensure satisfactory results. Some of these procedures were learned the hard way. Most important is that the epoxy cement be fresh. Precautions are necessary that the epoxy is not held too long prior to use, and even that the manufacturer does not ship a batch with very little of its normal shelf life left. Storage of epoxies at lower than room temperatures does help to minimize shelf aging. Second, the epoxies should be well mixed prior to use, otherwise the activator may segregate and incomplete curing will result. Third, precautions must be taken to prevent moisture pickup by the epoxy and this can be more of a danger if the epoxies are stored in a refrigerator. Fourth, the epoxies must be fully cured to have their full mechanical and electrical properties and be relatively free of subsequent changes. In this period, controls covering all of these points were set up. As a result there has been a gratifying improvement in the reliability of the gold epoxy grid contact.

D. Lamination Process

1. The Epoxy Cement

The experiences and comments on the gold epoxy cement as discussed above also apply to the clear epoxy cement used to attach the cover plastic. During the first half of this Contract period a poor experience with shelf stability was traced to a lot of epoxy cement which was over aged before being shipped by the vendor. It is not understood how the incomplete curing of the clear epoxy cement used to attach the cover plastic can affect the output of the CdS thin film solar cell, but there is very little doubt but that it does. Several epoxies have been evaluated for the cover plastic attachment, including a flexible epoxy but quite satisfactory results have been obtained with the present B-staging epoxy when it is properly used.

2. The Cell Cracking Problem

From the early days of the present plastic substrate CdS thin film cell design it has been noticed that there were numerous but nearly imperceptible cracks in the CdS layer. These cracks could be seen from the backs of the cells by looking at the cell with a glancing light reflecting from the cell at about 45°. The cracks look something like check cracks in dried mud. From the first, however, these cracks seemed to have no effect on the output of the cells, and hence very little attention was paid to them.

More recently it was suspected that these cracks might be affecting cell stability, hence they were examined in more detail. It was found that the cracks occurred in the cell gridding and lamination steps. Further investigation disclosed that they occurred during the heat-up portion of the gridding and lamination cycles. It had been the practice to place the laid-up cells between Teflon plastic sheets on an aluminum die, cover them with an aluminum foil diaphragm, evacuate the air from the underside of the diaphragm, apply 100 psi static pressure to the upperside of the diaphragm, heat the die to the desired temperature, hold for a set period, cool and then release the pressures and remove the cells.

It soon became evident that what was happening was that the 100 psi pressure clamped the cells between the aluminum foil diaphragm and the aluminum die, and that when the whole was heated to the 196°C gridding and/or laminating temperature the greater thermal expansion of the aluminum pulled the CdS film beyond its elastic limit and fractured the film. The cracks apparently caused no real difficulty as they would close when the cells cooled down again and the epoxy cement would tend to seal them. Electrical conduction in the CdS is mostly through the film to the substrate, hence the relatively wide crack spacing would have little effect here.

The cracks do give the cells a poor appearance and it is probable that they do hurt the electrical conduction of the CdS layer even if only slightly. It is also possible that they could hurt the long term stability of the cell, though it is also possible that they could help it, since it is in effect a type of stress relieving.

It was found that if the 100 psi laminating pressure was not applied until after the cells reached the 196°C temperature, the cracks did not occur. However, instead there was an increased incidence of wrinkles in the cells and in particular in the cover plastic and in the Teflon separating sheets (which would leave an impression in the cell). Also lower outputs of the cells were obtained due to start of cure of the epoxy before applying pressure.

A better method of alleviating these cracks was the substitution of a molybdenum or tantalum surface plate on the lamination die. The thermal expansion coefficients of these metals more nearly match that of the CdS. However, while alleviating the condition, this technique did not entirely cure it and some of these cracks are still obtained. It seems probable that the aluminum foil diaphragm at times will control the expansion and contraction of the cells rather than the base plate. The answer to this is probably the use of a lower pressure on the aluminum diaphragm, and there are other reasons that make this desirable.

3. Lower Lamination Pressure

In addition to contributing to the vertical cracks in the CdS layer, the high lamination pressure presses the grid into the CdS layer so firmly that the impression of the grid can clearly be discerned in the substrate plastic film when viewed from the back of the cell. Photomicrographs of cells which had degraded on thermal cycling disclosed lateral cracks in the CdS layer that appeared to result from stress concentrations which could have been transmitted via the grid itself. It is entirely possible that this occurs during the gridding or laminating steps and that this is then aggravated by the severe thermal conditions on the thermal cycling test.

Therefore, preliminary experiments were carried out to determine the practicality of gridding and laminating the cells with reduced pressure. Absolute pressures of 4, 15 and 25 psi in place of the standard 100 psi gage pressure were tried for both the gridding and lamination steps. There was some increased tendency for voids in the epoxy cover plastic adhesive to occur and for wrinkles in the package. However, with some special caution in laying up the package and placing it in the die, the use of thinner aluminum foil diaphragms, and the use of slightly thicker epoxy cement layers, successful laminations were carried out at pressures of 15 to 25 psi. These cells had much less tendency to form vertical cracks in the CdS, and left hardly any impression of the grid in the CdS layer or in the substrate plastic. Several of these cells were forwarded to Lewis Research Center, NASA, for evaluation and thermal cycling test. Further work along these lines is planned.

E. Cell Testing

1. I-V Characteristic Test Equipment

The solar simulator was rebuilt in the latter months of the period to give a system more in line with that being used at the Lewis Research Center. Sylvania "Sun Gun" lamps were substituted for the other tungsten filament lamps previously used, a new CuSO_4 solution water filter was installed with external means of cooling the solution, and a new vacuum hold-down fixture was designed and built. These changes, after elimination of the usual "bugs", have led to a much more dependable simulator, capable of handling a greater quantity of cells without overheating or loss of accuracy.

At the same time a new commercial electronic load was obtained and a better quality X-Y recorder. These permit much more rapid operation. From the experience of the first two months it appears that this new equipment setup is likely to be very much better with respect to the maintenance problems which have plagued us in the past.

2. Calibration

Calibration of light intensity of the solar simulator has on occasion been a problem. In two instances during the year the calibration of the test equipment was erroneous, and both times high values of cell output were obtained. In the second instance the error was nearly 8% high and it was more than 2 months before the error was found and corrected. (The efficiency figures quoted in this report have been corrected for these errors in so far as it has been possible to do so.) The error in this case was caused by the precision resistor that was wired across the standard airplane flown CdS cell increasing in resistance for some unknown reason. Steps have now been taken to have several secondary standard cells available and to cross-check these regularly to prevent a recurrence of this difficulty.

Except for the above-mentioned difficulties, the accuracy of measurement for the standard 3" x 3" CdS thin film solar cells has been reasonable, but has not as yet been precisely determined. On two separate "round robin" measurements of a group of 20 cells with the NASA Lewis Chemistry and Energy Conversion Division facility and the Lewis Lab Power Systems Division facility, the Clevite measurements checked the Lewis Laboratory measurements very closely. In addition, a group of 25 high efficiency cells checked on two occasions a month apart gave almost exactly the same outputs. A further check on the accuracy of the output measurements is obtained from the periodic measurements of cells on dry shelf storage. On the basis of all these measurements, it is believed that the relative accuracy for measurement of the Air Mass 1 conversion efficiency of standard 3" x 3" cells is within 2% - that is, a 5.0% cell if tested repeatedly at different times by different operators using the Clevite facility will give an indicated output of no more than 5.1% and no less than 4.9%.

3. Spectral Response Measurements

The indicated spectral response of CdS solar cells is very much a function of the conditions under which the measurements are taken. Practically all spectral response measurements that have been taken to date of CdS cells, and which have been reported in the literature or in various government contract reports, have been taken with conventional low light level monochromators.

Since there is a strong photoconductive component to the internal series resistance of the CdS cell, the magnitude of the current generated by any particular exciting light is very much a function of the total internal series resistance, including that portion of the resistance that is light sensitive. At low light levels, the internal series resistance can be very high. However, because of this photoconductive component, at higher and higher light levels, the series resistance is reduced greatly and gradually approaches an asymptotic value. The photoconductive component of the series resistance is believed to be due to copper impurity centers situated in the insulating region of the CdS and is responsive only to certain wavelengths of light.

In white light of sunlight intensity there would be enough of these wavelengths to completely excite these copper centers. Hence the internal series resistance would be nearly as low as it could be. Since the CdS cell would nearly always be used at sunlight intensity, this is the condition where the relative response of the cell to different wavelengths would be most meaningful.

A special monochromator has been designed and is now in the process of construction in our laboratory which will test the cells for relative spectral response at the high light levels of normal operation.

In the meantime, Figure 11 gives the spectral response of a recent vintage cell taken under the low illumination levels that have been used previously. The response under both monochromatic and monochromatic plus white light bias conditions are presented. These curves are very similar to earlier measurements, except that the cut-off at the short wavelength end is due to the Kapton cover plastic.

CELL N8IAK3 - 1 X 2 CM AREA ILLUMINATED

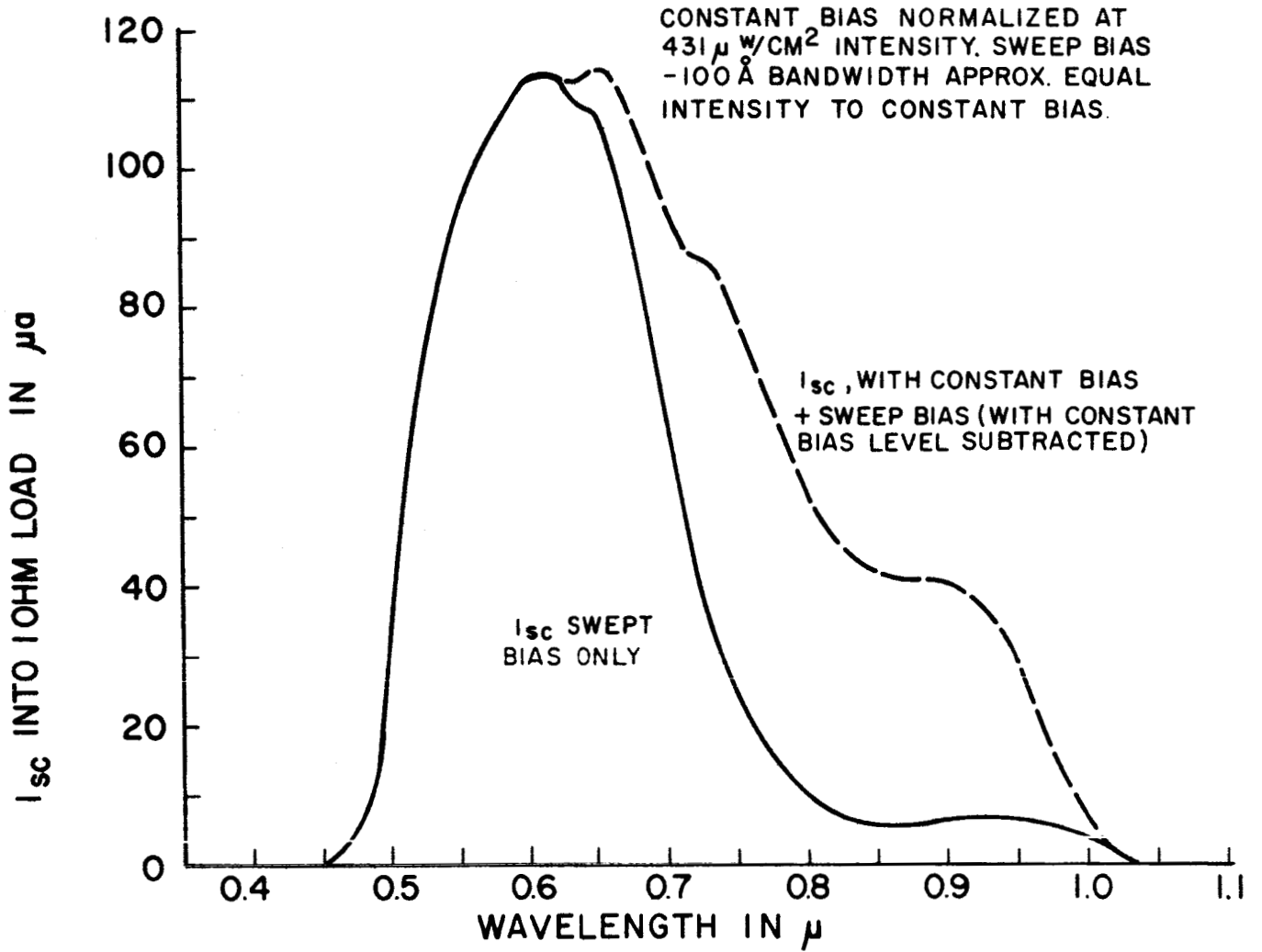


FIG. II : SPECTRAL RESPONSE OF KAPTON COVERED CELL .

REFERENCES

- 1 Contract NAS 3-2795. Final Report: W. J. Deshotels and F. Augustine, "Study of Thin Film Large Area Photovoltaic Solar Energy Converter", NASA CR 54343, October 30, 1964.
- 2 Contract NAS 3-6461. Final Report: F. A. Shirland, J. R. Hietanen, F. Augustine and W. K. Bower, "Development of Cadmium Sulfide Thin Film Photovoltaic Cells", NASA CR 54806, November 15, 1965.
- 3 Contract NAS 3-8502. Final Report: F. A. Shirland, J. R. Hietanen and W. K. Bower, "Study of Thin Film Large Area Photovoltaic Solar Energy Converter", NASA CR 72159, December 30, 1966.
- 4 L. R. Shiozawa, George A. Sullivan and Frank Augustine, "Research on the Mechanism of the Photovoltaic Effect in High-Efficiency CdS Thin Film Solar Cells", Aerospace Research Laboratory Technical Documentary Report ARL67-0190, September, 1967.
- 5 Adolph E. Spakowski, Ferdinand L. Acampora and Russell E. Hart, Jr., "Effect of Moisture on Cadmium Sulfide Solar Cells", NASA Technical Note TN D-3663, October, 1966.
- 6 Ref. 3, pgs. 26-7.
- 7 Ref. 2, pg 48.
- 8 Adolph E. Spakowski and John G. Ewashinka, "Thermal Cycling of Thin Film Cadmium Sulfide Solar Cells", NASA Technical Note TN D-3556, October, 1966.
A. E. Spakowski, A. E. Potter and R. L. Schalla, "Some Problems of the Thin Film Cadmium Sulfide Solar Cell", NASA Technical Memorandum TM X-52144, 1965.
- 9 A. G. Stanley, "Present Status of Cadmium Sulfide Thin Film Solar Cells", M.I.T. Lincoln Laboratory Technical Note 1967-52, 13 December 1967.
- 10 Ref. 2, pg 22.

QUALITY ASSURANCE PROGRAM

I. FABRICATION PROCESS

The CdS thin film fabrication process is basically a six-step process:

1. Substrate Preparation
 - A. Spraying
 - B. Burnishing
 - C. Zinc Electroplating
2. CdS Evaporation
 - A. Sintering
 - B. Crushing
 - C. Film Growth
3. Barrier Formation
 - A. CuCl Purification
 - B. Barrier Formation
4. Grid Attachment
 - A. Plating of Grids
 - B. Conductive Epoxy Application
 - C. Lamination
 - D. Bake-out
5. Cover Plastic Attachment
 - A. Lamination
 - B. Bake-out
6. Final Cell Preparation
 - A. Cleanup
 - B. Negative Tab Plating
 - C. Trimming

II. FABRICATION PROCESS INSPECTION

1. Inspection Procedures

Inspection steps are to be performed after each process step. These inspections will be performed in the main by a quality assurance inspector. He will be charged with the task of screening the cell for further processing. Other inspection steps will be performed by the Pilot Line operators as the cell proceeds through the various stages of the process. The full fabrication process inspection procedure is given below.

A. Substrate Inspection

(1) Spraying

Substrates are to be given a visual inspection and rejected for rough or uneven texture, the presence of foreign particles in the conductive layer, discoloration

of the back of the substrate as seen from the Kapton side of the substrate. With the aid of the light box the substrates are to be further inspected and rejected for the presence of pinholes or scratches in the plastic or conductive layer, excessive and/or nonuniform light transmission as compared with our standard comparison sample.

(2) Burnishing

Substrates to be rejected for resistance readings over 0.02Ω as per testing procedure A, nonuniform light transmission when compared with the standard comparison sample over the light box, and/or Ag Pyre-ML thicknesses under $0.002''$ or over $0.003''$ as tested per testing procedure B.

(3) Zinc Electroplating

Substrates to be rejected for the presence of fingerprints, pinholes or scratches through the zinc, water marks, stains or discolorations, adherent dust, and/or an irregular surface resulting from the zinc electroplate.

NOTE: Visual inspection steps will be made by comparing the substrate in question with standard visual comparison samples.

B. CdS Evaporation Inspection

(1) CdS Sintering

Sintered boules containing foreign inclusions or discoloration will be rejected.

(2) CdS Crushing

CdS powder that does not pass through a no. 42 mesh screen is to be rejected.

(3) CdS Film Growth

Films are to be rejected when the resistivity sample (per testing procedure C) is lower than 1Ω -cm and higher than 100Ω -cm, for pinholes, signs of nonadhering CdS, CdS particle splatter, irregular film growth, and the presence of foreign particles on the surface of the film.

C. Barrier Formation Inspection

(1) CuCl Purification

The presence of any brown, green or blue color in a batch of purified CuCl will be cause for rejection.

(2) Barrier Formation

Reject any barriered film having any peeled or chipped area in the active area of the cell, pinholes, any signs of copper precipitate in the active area of the cell, films less than $0.0008''$ thick as measured per testing procedure D, and/or films with an OCV voltage probe reading of less than 0.2 volts as measured per testing procedure E.

D. Grid Attachment Inspection

(1) Au Plating of Cu Grids

Reject all grids that are not completely covered by gold, any showing discoloration.

(2) Application of the conductive epoxy to the grids

Reject any grid which has any areas showing where there is no gold conductive epoxy or any area where the gold epoxy coating is lumpy due to too much gold epoxy.

(3) Grid Lamination

Reject any gridded cell having any areas of loose nonadhering grids, torn or ripped grid wires, torn cell tabs, grid misalignment, and/or any gold epoxy smeared on the cell surface.

(4) Grid Bake-out

Reject any gridded cells having poorly adhering grids, torn or ripped wires, and/or torn cell tabs.

E. Cover Plastic Attachment Inspection

(1) Cover Plastic Lamination

Reject all cells having any tears in the plastic or the tabs, voids, delamination, cover plastic misalignment, cover plastic tearing, and/or cell curl of more than 1/4".

(2) Cover Plastic Bake-out

Reject cells having any tears in the plastic or the tab, voids, delaminations, cover plastic tearing, and/or cell curl of more than 1/4".

F. Final Cell Preparation Inspection

(1) Cell Cleanup

Reject cells showing any signs of delamination, tearing of cell or tabs, excessive epoxy on the tabs or plastic, and/or improper cell dimensions on either tab edge.

(2) Negative Tab Plating

Reject any cell having discolored tabs and/or tabs having any non-plated areas.

(3) Cell Trimming

Reject cells having improper dimensions.

A final visual cell inspection will be made before the cell electrical tests and cells will be rejected if any of the following are present:

1. Peeling cover plastic
2. Torn positive or negative tab
3. Improperly applied grids (wrinkled, torn, misaligned, etc.)
4. Chipped or peeled CdS film
5. Excessive curl where the curl height exceeds 1/4"
6. Voids
7. Included foreign bodies, dents, wrinkles, scratches, etc.
8. Improper cell dimensions

A final electrical cell inspection will be made and cells will be rejected if any of the following are present under the standard test conditions of 100 mw/cm² at 25°C:

1. Mylar covered cells showing less than 4.1% conversion efficiency.
2. Kapton covered cells showing less than 3.3% conversion efficiency.

III. INSPECTION RESPONSIBILITIES

1. Quality Assurance Inspector

A. Basic Component Chemicals and Parts

All incoming materials to be inspected and tested to insure they meet all cell component specifications. (See IIIA for specific specifications.)

B. Sprayed Layer

- (1) Texture
- (2) Discoloration (back and front)
- (3) Foreign particle inclusions
- (4) Pinholes or scratches
- (5) Uneven light transmission
- (6) Blistering

C. Burnished Layer

- (1) Texture
- (2) Discoloration (back and front)
- (3) Foreign particle inclusions
- (4) Pinholes or scratches
- (5) Uneven light transmission
- (6) Blistering

D. Zinc Layer

- (1) Fingerprints
- (2) Pinholes or scratches thru zinc
- (3) H₂O marks
- (4) Stains or discolorations (back and front)
- (5) Foreign particle inclusions
- (6) Uneven zinc plating

E. CdS Film

- (1) Excessive pinholes
- (2) Film adherence
- (3) Particle splatter
- (4) Nonuniform film growth
- (5) Excessive foreign particles

F. Barriered Film

- (1) Film Adherence (peeling or chipping)
- (2) Excessive pinholes
- (3) Copper precipitation
- (4) OCV probe measurement

G. Gold Plated Grids

- (1) Uncovered areas
- (2) Discoloration
- (3) Broken or wrinkled wires

H. Epoxy Coated Grids

- (1) Excessive epoxy
- (2) Insufficient epoxy
- (3) Bare spots
- (4) Wrinkled grids
- (5) Torn grids

I. Final Inspection

- (1) Peeling plastic
- (2) Torn contacts
- (3) Improperly applied grids (torn, wrinkled, etc.)
- (4) Peeled CdS film
- (5) Excessive curl
- (6) Voids
- (7) Excessive inclusions
- (8) Improper dimensions
- (9) Kapton covered cells less than 3.3%
- (10) Mylar covered cells less than 4.1%

IIIA. CELL COMPONENT SPECIFICATIONS

Materials used in the construction of CdS thin film solar cells shall meet the following specifications:

1. Kapton Substrate Material

100XH667 Kapton Polyimide film type H supplied by I. E. DuPont de Nemours & Company, Inc., Film Dept., Chestnut Run Laboratory, Wilmington, Delaware.

- A. Film supplied on 3" dia., 1/4" hard paper core
- B. Film thickness tolerance $0.001'' \pm 0.0001''$ as measured on optical micrometer.

- C. Film must be transparent and have uniform yellow color.
- D. Film must be pinhole free, free of wrinkles, tears, pits or dents.
- E. Film shall be free of dust, dirt, fingerprints, and other foreign matter.

2. Silver Powder

Ag powder, flake, MD 750-Metals Disintegrating Corp., Elizabeth, N. J.

- A. To be received in polyethylene bag in metal container labeled with --
 - grade
 - Lot number
 - date
- B. Powder is to have uniform color and be free of agglomerations.
- C. Silver powder is to be free of magnetic particles.

3. Pyre-ML Varnish

Pyre-ML Varnish (RK-692) - E. I. DuPont de Nemours & Company, Inc.,
 Fabrics and Finishes Dept., Wilmington, Delaware.

- A. Pyre-ML to be received in polyethylene containers.
- B. Clear and dark amber in color with following properties:
 - (1) wt/gal. 8.54 + 0.05 lbs.
 - (2) % solids 12.5 - 13.5%
 - (3) viscosity at 25°C 6-10 poises
 - (4) flash point 37°C (open cup)
- C. Varnish to be stored in closed container at maximum of 40°F (4, 4°C)
 to insure 12 month stability (77°F (20°C) stability is 3 mos., 120°F (49°C) is 10 -
 12 days).

4. Zinc Electroplate

Zinc electroplate coated substrate must pass zinc electroplate inspection.

5. CdS Raw Material

Type 118-8-2 CdS Electronic Chemical - G.E. Co., Cleveland, Ohio,

- A. Material to be furnished in brown colored, #5, sealed glass containers.
- B. Orange-yellow color, granular and dry.
- C. Material to be given the standard semiquantitative spectrographic analysis showing % of Al, Cd, Cu, Fe, Mg, Ni and Si. Reject material if it does not meet standard manufacturer's guaranteed specification.
- D. Material to be evaporated as per standard process; films to be processed and tested according to standard procedures. If acceptable cells produced, material to be dated and stored for use.

6. Barrier Layer

Barrier layer must pass barrier layer inspection.

7. Cu Grids

Etched Cu grid made from .00045 + .00005" thick copper foil 99.9% min. purity, Runchi rule 60 lpi x 10 lpi @ integral tab per Drawing No. C-001B (Hamilton Watch Company, Lancaster, Pa.)

A. Grids to conform to Drawing C-001B are received in packages with individual paper separators.

B. Check 5 to 10 grids from each shipment for thickness. If one is out of specification, inspect 100%.

C. 100% visual inspect and reject any grids with --

(1) over 5 broken wires per grid

(2) wrinkles that may cause grid to fold and/or wrinkle in processing

(3) any tears

(4) any photo resist

(5) poorly etched grids causing poor appearance and/or light transmission

(6) any grease, fingerprints, or badly stained or discolored grids

D. All lots to have following inspection data:

(1) thickness

(2) visual inspection results

8. Au Electroplated Grid

Au electroplate grids must pass Au electroplated grid inspection.

9. Au Epoxy

Gold filled conductive epoxy #3205 - Epoxy Products Co., New Haven, Conn.

A. Au epoxy to be supplied in 1 oz. glass jars.

B. Epoxy to be stored under refrigeration (at 40°F shelf life is 6 mos.)

C. Allow epoxy to reach room temperature before opening container.

10. Epoxy Coated Mylar and/or Kapton

Mylar and/or Kapton to be coated by vendor with Astro Epoxy.

A. Vendor to obtain plastic material and adhesive.

B. Vendor to coat and dry plastic film. Adhesive dry film thickness to be 0.00055 in. ± 0.00005 in:

C. Adhesive coated plastic film to be wrapped on 3 inch paper core and interleaved with polyethylene film to prevent sticking between wraps.

11. Au Electroplate Negative Tab

Au electroplate on negative tab must pass negative tab inspections after Au electroplate is applied.

III. INSPECTION RESPONSIBILITIES - cont'd

2. Individual Pilot Line Operators

A. Substrate Preparation Operator

(1) Kapton Substrate (before spraying) (Visual Inspection)

(a) Pinholes

(b) Wrinkles

(c) Tears

- (d) Pits or dents
 - (e) Dust
 - (f) Dirt
 - (g) Fingerprints
 - (h) Other foreign matter
- (2) Silver Powder (before mixing) (Visual Inspection)
- (a) Uniform color
 - (b) No agglomerates
- (3) Pyre-ML Varnish (before mixing)
- (a) Clear and dark amber color
 - (b) Proper storage conditions
 - (c) Viscosity
- (4) Conductive Spray Layer (after cure) (Visual Inspection)
- (a) Texture
 - (b) Blistering
 - (c) Discoloration thru back
 - (d) Discoloration of layer
 - (e) Foreign particle inclusion
 - (f) Pinholes
 - (g) Scratches
- (5) Burnished Layer (after burnish)
- (a) Resistance measurement
 - (b) Thickness measurement
 - (c) Visual of same points under (4) above
- (6) Zinc Electroplated Layer (after plating) (Visual Inspection)
- (a) Fingerprints
 - (b) Pinholes thru zinc
 - (c) Scratches thru zinc
 - (d) Watermarks
 - (e) Stains
 - (f) Adherent foreign particles
 - (g) Uneven zinc
- B. CdS Film Evaporation Operator
- (1) Sintered CdS
- (a) Color
 - (b) Foreign inclusions
- (2) Crushed CdS
- (a) Powder size
- (3) Zinc Plated Conductive Substrate
- (a) Major visual flaws
 - (b) Discoloration
 - (c) Foreign particles and dust
- (4) CdS Evaporated Film
- (a) Film resistivity
 - (b) Major pinholes or scratches
 - (c) Adherence
 - (d) Color
 - (e) Excessive splatter
 - (f) Texture

- C. Barrier Application Operator
 - (1) Purified Cu Cl
 - (a) Color
 - (b) Texture
 - (2) Barriered CdS Film
 - (a) Peeling or chipping
 - (b) Major pinholes
 - (c) Copper precipitate
 - (d) Film thickness
 - (e) General coloring
- D. Gridding and Packaging Operator
 - (1) Epoxied Grids
 - (a) Coverage uniformity
 - (b) Thickness
 - (c) Discoloration
 - (d) Wrinkled, tears or rips
 - (2) Laminated Grids
 - (a) Adherence
 - (b) Tears, rips or wrinkles
 - (c) Torn tabs
 - (d) Grid alignment
 - (e) Excessive epoxy
 - (f) Insulator strip alignment
 - (3) Baked-out Grids
 - (a) Adherence
 - (b) Tears, rips or wrinkles
 - (c) Torn tabs
 - (d) Grid alignment
 - (e) Excessive epoxy
 - (f) Insulator strip alignment
 - (4) Epoxy Covered Cover Plastic
 - (a) Epoxy coverage
 - (5) Laminated Cover Plastic
 - (a) Plastic tears or wrinkles
 - (b) Tab tears
 - (c) Alignment
 - (d) Voids
 - (e) Delamination
 - (f) Curl
 - (6) Baked-out Cover Plastic
 - (a) Plastic tears or wrinkles
 - (b) Tab tears
 - (c) Alignment
 - (d) Voids
 - (e) Delamination
 - (f) Curl

E. Final Preparation Operator

- (1) Cell Cleanup
 - (a) Delamination
 - (b) Tearing
 - (c) Epoxy on tabs
 - (d) Epoxy on plastic
 - (e) Dimensions

- (2) Tab Plating

- (a) Thin plating
- (b) Uneven plating
- (c) Discoloration

- (3) Cell Trimming

- (a) Dimensions

F. Cell Tester

- (1) General Inspection

- (a) Peeled plastic
- (b) Torn contacts
- (c) Wrinkled, torn or ripped grids
- (d) Peeled CdS
- (e) Excessive curl
- (f) Voids
- (g) Excessive inclusions
- (h) Improper dimensions
- (i) Kapton covered cell efficiency minimum
- (j) Mylar covered cell efficiency minimum

3. Pilot Line Supervisor

A. Process Chemical and Solution Control

- (1) Ag Pyre-ML Spray Mixture

- (a) Mix in accordance with Process Specification.
- (b) Mix well with magnetic stirrer - if gelling occurs, dispose of solution.
- (c) Keep solution stored in refrigerator on week ends in sealed container.
- (d) Mix well before using.

- (2) Zinc Plating Solution

- (a) Mix in accordance with Process Specification.
- (b) Keep bath within specified operating limits by initial and weekly chemical analysis.
- (c) Adjust bath parameters to meet specified operating limits.

- (3) CuCl Purification

PROPRIETARY

- (4) Gold Plating Solution

- (a) Mix in accordance with Process Specification.
- (b) Keep bath within specified operating limits by initial and bi-weekly chemical analysis.

- (c) Adjust bath parameters to meet specified operating limits.
- (d) Bath clarity to be observed and maintained by filtration as becomes necessary.
MINIMIZE DRAG OUT LOSS.

(5) Alconox Solution

Alconoc, laboratory detergent, Alconox, Inc., Plainview, N. Y.

- (a) Free flowing white powder packaged in resealable fibre container.
- (b) Mix according to Process Specification
DO NOT USE MORE THAN ONE WORK WEEK
Change more frequently if needed.

(6) Alkaline Cleaning Solution

Sodium Cyanide - tech. grade

Sodium Hydroxide - tech. grade

- (a) Mix according to Process Specification.
- (b) Keep solution at room temperature
- (c) Keep away from acid solutions.

(7) Acid Cleaning Solution

Diversey Cleaner #914 liquid concentrate, Diversey Corp.,
Chicago, Illinois.

- (a) Mix according to Process Specification.
- (b) Maintain solution concentration at 20% \pm 5% by volume.

Test: Use 10 ml and titrate with 0.25
N NaOH with phenolphthalin (mls of
0.25 N NaOH x 0.54 = conc % vol)

Add concentrated Diversey Cleaner to
raise solution concentration.

Add dimineralized H₂O to lower concentration.

- (c) Make tests minimum of once a week.
- (d) Replace solution after maximum of 1000 grids or
after two weeks.
- (e) Replace more often if necessary.

(8) Copper Sulfate Solution Filter

- (a) Mix in accordance to Process Specification.

(9) Alcohol Rinse Solution

- (a) Change at the beginning of each work week.
- (b) Change more frequently if necessary.
- (c) Alcohol in wash bottle to be changed daily.

(10) Barrier Pre-etch Solution

PROPRIETARY

(11) Barrier Solution

PROPRIETARY

- (12) Water Rinse Solutions
 - (a) All H₂O rinse solutions are continuous flow solutions.
 - (b) All H₂O rinse solutions consist of tap H₂O.
 - (c) Line filters are to be checked monthly.
- (13) Demineralized H₂O
 - (a) Used in barrier and etch solution, Au and Zinc electroplating solutions, etc.

Chemicals and supplies used in the various fabrication processes are to meet the specifications set down for them in the Pilot Line Process Specifications. The Pilot Line Supervisor will be responsible for the assurance that these specifications are met.

B. Hardware Specifications

Substrate Preparation

- (1) Silver Pyre-ML Spray Mixture
 - (a) 600 ml Pyrex Brand Glass Beaker
 - (b) Glass stirring rod
 - (c) Glass bottle
- (2) Silver Pyre-ML Application
 - (a) Rubber gloves
 - (b) Aluminum board
 - (c) Type 900-S Kim-wipes
 - (d) Clips
- (3) Burnishing
 - (a) Glass plates
 - (b) #202, 3/4" Scotch brand masking tape
 - (c) Single-edge industrial blade
 - (d) #448 Scotch brite ultra-fine cleaning and finishing pads
 - (e) Type 900-S Kim-wipes
 - (f) Rubber gloves
 - (g) Punch
- (4) Zinc Plating Solution
 - (a) 18" x 12" x 18" Polyethylene tank
 - (b) pH paper
- (5) Licorice Solution
 - (a) Glass beaker
 - (b) Filter paper
 - (c) Glass bottle
- (6) Alconox Solution
 - (a) Glass beaker
- (7) Water Rinse Solution
 - (a) Polyethylene tank
- (8) Alcohol Rinse Solution
 - (a) Polyethylene tank
 - (b) Spray bottle

- (9) Zinc Electroplating
- (a) No. 3-535 Fisher Brush, Tynex bristles
 - (b) Substrate carrier fixture
 - (c) Plastic mask and clamps
 - (d) Plastic sheet
 - (e) Cardboard
 - (f) Paper clips
 - (g) Single edge industrial blades
 - (h) pHydrion Paper (3.0-5.5), Micro Essentials Laboratory, Brooklyn, N. Y.

Evaporation

(1) CdS Sintering

- (a) Plastic foil

(2) CdS Crushing

- (a) Mortar and Restle
- (b) #42 Tyler screen
- (c) Glass jar

(3) Evaporation (Vertical NRC)

- (a) Fiberfrax (0.040" thick)
- (b) Scotch brite cleaning pad
- (c) Evaporation sources
- (d) Screens
- (e) Tweezers
- (f) Marking pen

(4) Evaporation (Horizontal NRC)

- (a) Quartz wool
- (b) Scotch brite cleaning pad
- (c) Evaporation boats
- (d) Evaporation sources
- (e) Gloves
- (f) Tweezers
- (g) Marking pen

Barrier Application

(1) CuCl Preparation

PROPRIETARY

(2) Barrier Formation

PROPRIETARY

Gridding and Packaging

(1) Gold Plating Solution

- (a) Platinum anode
- (b) One liter Pyrex beaker
- (c) pH paper
- (d) Polyethylene tank

(2) Water Rinse Solution

- (a) Polyethylene tank

- (3) Acid Cleaning Solution
 - (a) One liter beaker
- (4) Alkaline Cleaning Solution
 - (a) Glass beaker
- (5) Gold Plating of Grids
 - (a) Plating racks
 - (b) Glass beaker
- (6) Epoxied Grid
 - (a) 1/8" Silicone rubber sheet
 - (b) 3 mil Teflon sheet
 - (c) Stainless steel spatula
 - (d) Hard surfaced roller
 - (e) Shallow plastic box
- (7) Epoxied Insulation Strip
 - (a) Scotch wipes #590
 - (b) Scotch masking tape, #202, 3/4"
 - (c) Cardboard, smooth surface
- (8) Grid Lamination
 - (a) 3 mil Teflon sheet
 - (b) H-18 grade aluminum foil (3 ml), Reynolds Aluminum Co.
 - (c) Tank Nitrogen (water pumped)
 - (d) Lucite transfer plate
 - (e) Glass plates
 - (f) Rubber gasket
 - (g) Spring clamp
- (9) Cover Plastic Lamination
 - (a) Teflon plastic sheet (3 mil)
 - (b) H-18 grade Aluminum foil (3 mil) Reynolds Aluminum Co.
 - (c) Tank nitrogen (water pumped)
 - (d) Lucite transfer plate
 - (e) Glass plates
 - (f) Rubber gasket
 - (g) Spring clamp

C. Chemical Specifications

Substrate Preparation

- (1) Silver Pyre-ML Spray Mixture
 - (a) AR Grade, N, N-Dimethyl formamide
 - (b) AR Grade Toluene
- (2) Silver Pyre-ML Application
 - (a) AR Grade N, N-Dimethyl formamide
- (3) Burnishing
 - (a) AR Grade Methanol (Anhydrous)

- (4) Zinc Plating Solution
 - (a) AR Grade ammonium chloride
 - (b) Crystal technical grade ammonium fluoborate
(General Chem. Code 1273)
 - (c) AR grade (29% NH₃) ammonium hydroxide
 - (d) 48% AR grade fluoboric acid
 - (e) Licorice per Process Solution Specification
 - (f) Zinc fluoborate (40% solution) #2443, General
Chemical, Cleveland, Ohio
 - (g) Technical grade zinc carbonate (powder)
 - (h) Demineralized water
 - (i) Zinc oxide

- (5) Licorice Solution
 - (a) Licorice root USP powdered (compound Senna
Powder NFX1) S. B. Penick & Co., distributed
by Norwood Drug, Inc.
 - (b) Demineralized water
 - (c) AR grade (29% NH₃) ammonium hydroxide

- (6) Alconox Solution
 - (a) Alconox, laboratory detergent, Alconox, Inc.,
Plainview, N. Y.
 - (b) Tap water

- (7) Water Rinse Solution
 - (a) Tap water

- (8) Alcohol Rinse Solution
 - (a) AR grade methanol (anhydrous)

- (9) Zinc Electroplating
 - (a) Zinc plating solution per Process Solution Specification
 - (b) Alconox solution per Process Solution Specification
 - (c) Tap water
 - (d) AR grade methanol (anhydrous)

Evaporation

- (1) CdS Sintering
 - (a) Argon

- (2) CdS Crushing
 - None

- (3) Evaporation (Vertical NRC)
 - (a) AR grade methanol
 - (b) AR grade hydrochloric acid

- (4) Evaporation (Horizontal NRC)
 - (a) AR grade methanol
 - (b) AR grade hydrochloric acid

Barrier Application

(1) CuCl Preparation

PROPRIETARY

(2) Barrier Formation

PROPRIETARY

Gridding and Packaging

(1) Gold Plating Solution

- (a) Gold electroplating solution, Temperex HD, Sel-Rex Corp, Nutley, New Jersey
- (b) Acid pH adjusting salt for Temperex HD process, Sel-Rex Corp.
- (c) Base pH adjusting salt for Temperex HD process, Sel-Rex Corp.

(2) Water Rinse Solution

- (a) Demineralized water

(3) Acid Cleaning Solution

- (a) Diversey Cleaner #914 liquid concentrate, Diversey Corp., Chicago, Illinois
- (b) Demineralized water
- (c) 0.25N NaOH
- (d) Phenolphthalin

(4) Alkaline Cleaning Solution

- (a) Technical grade sodium cyanide
- (b) Technical grade sodium hydroxide

(5) Gold Plating of Grids

- (a) Alkaline cleaning solution
- (b) Acid cleaning solution
- (c) Temperex HD gold plating solution
- (d) AR grade methyl alcohol (anhydrous)
- (e) Demineralized water
- (f) Tap water

(6) Epoxied Grid

None

(7) Epoxied Insulation Strip

- (a) Technical grade MEK
- (b) AR grade acetone

(8) Grid Lamination

None

(9) Cover Plastic Lamination

None

D. Pilot Line Equipment Maintenance

(1) Substrate Preparation

- (a) Spray Hood
Filter
Air Pull
- (b) Spray gun
Daily care
Tear down
- (c) Drying oven
General
- (d) Curing oven
- (e) Thickness measuring equipment
- (f) Resistivity equipment
- (g) Solution tanks
- (h) Electrical controls
- (i) Drying oven
- (j) Storage box

(2) Evaporation

- (a) Evaporation
Pumps
Controls
Tooling
- (b) Mesh screens
- (c) Mortar and pestle

(3) Barrier

PROPRIETARY

(4) Lamination

- (a) Laminating presses
- (b) Vacuum ovens
- (c) Desiccator storage
- (d) Soldering iron
- (e) Cutting

(5) Final Preparation

- (a) Au and Cu tanks
- (b) Electrical tanks

(6) Testing

- (a) Testing equipment