THIRD QUARTERLY TECHNICAL PROGRESS REPORT

on

INVESTIGATION OF THIN FILM CADMIUM SULFIDE SOLAR CELLS

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R. J. Humrick
R. F. Belt

SOLID STATE RESEARCH LABORATORY
CRYSTAL-SOLID STATE DIVISION
THE HARSHAW CHEMICAL COMPANY
1945 E. 97th Street
Cleveland 15, Ohio

PERIOD OF 26 MAY 1964 to 25 AUGUST 1964

9 August, 1964

Contract No. AF 33(615)-1248
Task No. 817301-32

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RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE
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NOTICES

FOREWORD

This report was prepared by The Harshaw Chemical Company, Solid State Research Laboratory, covering the work accomplished during the period from May 26, 1964, to August 25, 1964, under Contract AF 33(615)-1248. This report is being published and distributed prior to Air Force review. Its publication is for the exchange and stimulation of ideas and does not constitute approval by the Air Force of the findings or conclusion contained therein.

The work of this project deals with certain specific problem areas of the cadmium sulfide thin film front wall solar cell. Related contracts sponsored by the Air Force, by other Department of Defense Agencies, and by NASA at Harshaw and at other organizations are concerned with other aspects of cadmium sulfide solar cells, other photovoltaic conversion systems and with the investigation of the properties of various semiconductive materials with photovoltaic possibilities.

The contract is being monitored by Mr. L. D. Massie, APIP-2, Project Engineer, Air Force Aero Propulsion Laboratory of the Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio. The detailed work of the project has been divided into two major sections with a principal investigator in charge of each. Cell development efforts have been under the supervision of R. J. Humrick including work on junction formation technique, accelerated UV tests, contacting techniques, radiation damage, new cell design, cells and arrays and pilot line. Mr. Humrick has been assisted by B. G. Keramidas, and W. W. Baldauf and D. J. Harvey. Cell research efforts on evaporation parameters, inhibition of efficiency decay, barrier studies, and theoretical studies has been conducted by R. F. Belt, as the principal investigator and assisted by E. R. Hill, D. Krus, K. Tokunaga and D. Dickey. Technical and administrative direction of the project has been carried out by J. C. Schaefer.

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INTRODUCTION AND SUMMARY

This program is a continuation of the research and development on large area, thin film flexible, light weight cadmium sulfide solar cells.

High efficiency stable cells with improved power to weight ratios are goals of this investigation. Attainment of these goals encompasses several areas of investigation which must be pursued simultaneously.

The degradation of electroplated cells has been closely observed and it has been found that recovery can be accomplished under proper conditions. Chemical milling of the substrate is an excellent method for producing high power to weight ratio cells.

Fabrication of the one-half and one square foot mechanical sample arrays indicate improved total area utilization factors.

Photovoltaic cells and diodes have been prepared by first depositing a thin film of CuCl on CdS. The CuCl was subsequently converted to $Cu_{9,5}S_5$ by means of H_2S.

Optical studies on electroplated and chemiplated barriers have served to confirm the presence of Cu_2S alone or mixed with CuS.

Thin layers of SiO have been utilized as a water vapor barrier to significantly decrease degradation of cells.

Additional theoretical work has been performed on a heterojunction model of the cell operation.

PART I - CELL DEVELOPMENT

JUNCTION FORMATION TECHNIQUE

Electroplated Barrier

A stable formation of the barrier layer is essential to the initial quality of the CdS thin film cell as well as assuring the quality after long periods of storage.

The electroplated barrier formation has been standardized to give the desired properties of high efficiency and good stability.

It has been noted during recent months that the cell efficiency has gradually decreased for reasons difficult to ascertain. The entire procedure has come under close scrutiny and it has become obvious that a definite change in the procedures or use of equipment has inadvertently been incorporated.

Several avenues have been followed to determine the actual cause of this low efficiency. The film formation, barrier formation and subsequent treatments after formation can be the cause either separately or in conjunction with one another. The film formation was the chief suspect since this procedure is the most difficult to control. Exhaustive examinations and observations of the process failed to reveal defects. The plating bath was the next item investigated. The transistor washer was investigated at the same time because of its use in removing excess plating bath remaining on the barrier surface. Abnormalities were discovered in both phases of the barrier formation. The transistor washer was completely out of commission for a total of two weeks. The water had become contaminated from an unknown source and was partially rectified after the complete system was taken apart and cleaned. In addition, the conditioning of the plating solution was found to be inadequate. To confuse the issue even more, the pressure test unit employed in observing the I-V cell characteristics had been performing erratically during this same period. The test fixture was redesigned to reduce the series resistance found in the I-V characteristic curve.

After these malfunctions were resolved, the average efficiency was found to be below normal. The efficiency loss was essentially equivalent to the increase attributed to the transistor washer and its introduction into the cell fabrication procedure. As of this writing large quantities of a fungus have been found in the system and steps are being taken to remove same. Results of this procedure are at present unknown but it is anticipated that the outcome will be highly favorable in restoring the efficiency level of the cells to their previous value or better.

A group of electroplated cells have been observed during the last six months to check the effectiveness of storage under supposedly proper conditions. The original average efficiency of the group of nine cells was 3.1%.

After a period of 13 weeks of desiccation, the efficiency dropped to about 2.0%. This rate of degradation should never have occurred. Although the desiccant appeared to be in excellent condition, new desiccant was inserted in the chamber and after repeated changes of desiccant, the efficiency rose to a 2.5% average. Insertion of these cells into a vacuum chamber for a few days brought the average efficiency up further to 2.7%. After removal from the vacuum chamber, the cells have been stored in a desiccated vacuum chamber. The efficiency has remained at a steady 2.6% which is about 15% below the original values measured six months ago. Figure I is a graph of the short circuit current, open circuit voltage and efficiency during this period of time. The sharp excursion of the graph occurred when the samples were placed in the vacuum chamber and evacuated for several days. This observation shows that under proper conditions, the recovery of degraded cells can be readily affected. This is of extreme importance when considering these cells for space power applications. If any given cell unit degrades during storage, it can be expected to recover rapidly after launching.

Cells fabricated in February 1963, are also under observation. These have been exposed to ambient laboratory conditions for one and one-half years. Several of these cells had degraded severely in this period and recovery of these cells was attempted. The cells were placed in a desiccated chamber for several days and then in a bell jar for exposure to lower pressures. Complete information on their recovery rate is not available as yet, but several cells are improving, but others are not doing as well.

Chemiplated Barrier

The dependence of short circuit current, open circuit voltage and conversion efficiency of chemiplated cells on the time of heat treatment and on the gaseous environment of heating was investigated. The temperatures chosen for heat treatment of cells were 150°C, 200°C, 250°C and 300°C. The environments for each of the temperatures were: vacuum, dry air, nitrogen, argon, oxygen and hydrogen gases.

The general effect of heat treatment on the performance of chemiplated cells is the increase of the conversion efficiency. This increase is due to the rise of the value of the open circuit voltage and the consequent improvement of the fill factor which may improve as much as 100% over its original value. An undesirable outcome of the heat treatment is the loss of short circuit current which accompanies the above mentioned changes in most cases.

From the data compiled thus far, it appears that the heat alone is responsible for the improvements in the performance of the cells. The temperature of the furnace determines the rate of the reaction taking place in the barrier layer. The time of heat treatment must be controlled, accordingly becoming shorter as the temperature of the environment is set at higher values.

The improvement of the I-V characteristics resulting from the heat treatment occurs during the first few minutes of the exposure. The values thus attained are not altered if the heat treatment is prolonged. Only if the heat treatment is prolonged to five times that which is normally required, the shunt resistance begins to decrease and the value of the fill factor deteriorates rapidly.

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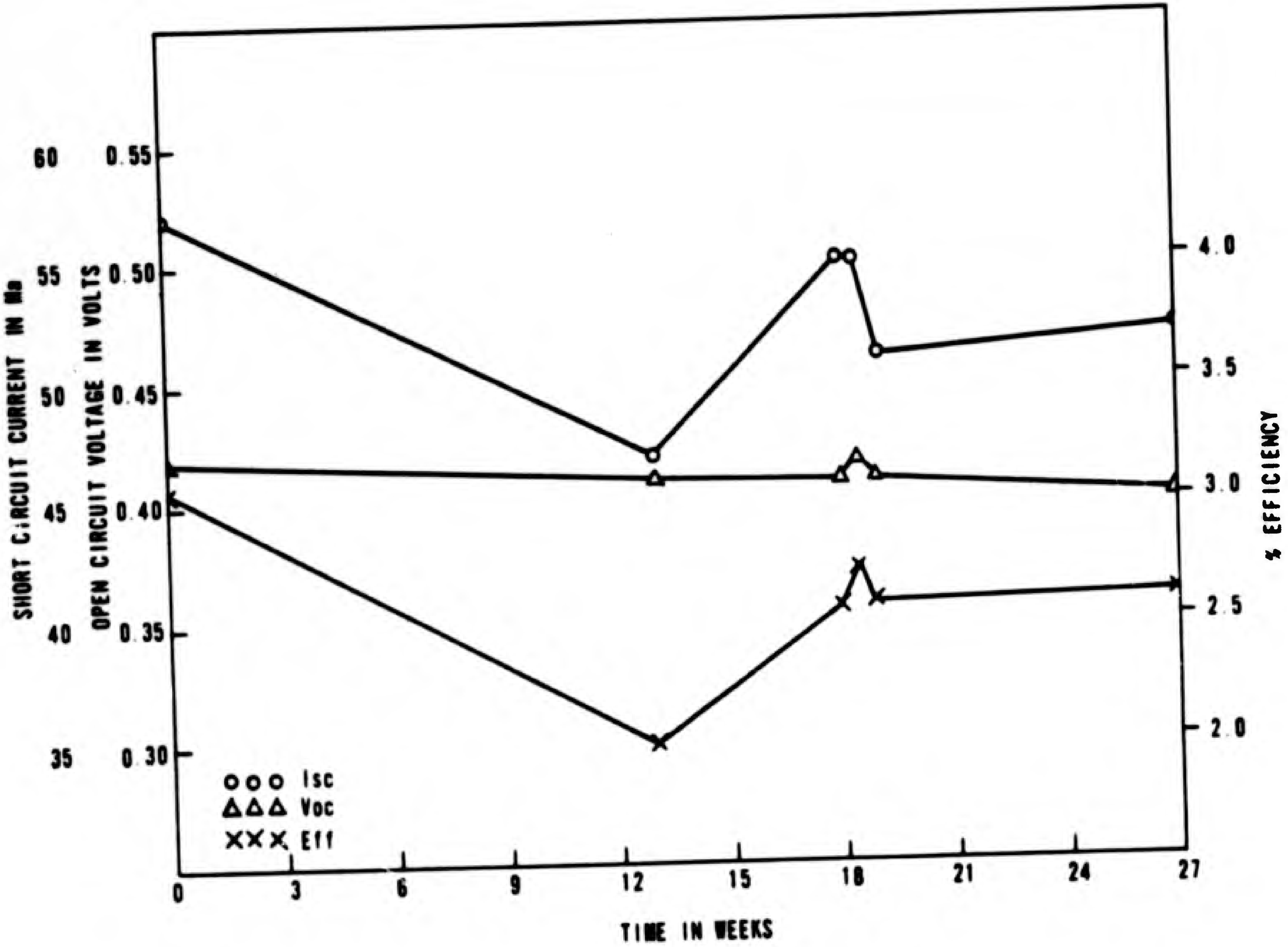

Fig. 1   Degradation Curve of Nine Electroplated Cells

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Until now, only cuprous chloride was used in "solution" to provide the Cu+ ions necessary for the formation of the barrier layer. But other copper salts such as cuprous bromide, cuprous iodide, and cuprous sulfite have solubilities greater than that of CdS and they would be used as sources of the needed Cu+ ions. Aqueous "solutions" of all these salts were made and barrier layers were formed by immersion of CdS thin films into them. Because all three salts are insoluble in water the times of immersion had to be considerably prolonged. The values of the open circuit voltage of cells made by immersion into the above mentioned "solutions" are comparable to those of the cells made in CuCl "solutions" but the values of the short circuit current are much lower.

The possibility of etching the surface of the polycrystalline CdS thin films prior to the formation of the barrier was investigated. The thin films were etched in concentrated or slightly diluted solutions of HCl and then immersed into the CuCl "solution" for the formation of the barrier. The data compiled thus far seem to indicate that the preliminary etching enhances the value of the short circuit current. The pilot line for making CdS cells by the method of direct chemical deposition is being continued with emphasis on 2" x 2"'s and 3" x 3"'s.

The average values are .42 for the open circuit voltage, 10.0 ma/cm^2 for the current densities and 2.80% for the efficiencies. The lower than usual values of the average current density and efficiency are primarily due to the fact that some films were poorly adhered on the molybdenum substrate and consequently gave cells of poor performance.

The stability samples, the degradation rate of which was reported in the previous quarterly report(1), show an improvement in their efficiency. The open circuit voltage remains constant. The short circuit current regains its value and is responsible for the rise of the value of the efficiency. The variation of the open circuit voltage, short circuit current and efficiency of a representative sample are shown in Figure 2.

In addition to the stability samples kept under desiccated conditions, other samples were placed in room environment and are being observed. Taking into consideration the fact that the humidity of the laboratory room varies considerably, the performance of the cells can be considered very satisfactory. Figures 3,4,5, and 6 show the variations in open circuit voltage, efficiency and current density for some characteristic samples.

The performance of both chemiplated and electroplated cells stored in environments of various relative humidities will be investigated further during the next quarter using saturated solutions of various salts; desired values of relative humidities can be achieved and the degradation rate of cells stored in such environments will be followed closely.

ACCELERATED ULTRAVIOLET TESTS

The objective of this protion of the program is to expose cells and cell materials to the ultraviolet radiation equivalent of one year of space exposure. These tests are to be of an accelerated nature.

The lamp used for obtaining the necessary radiation was a General Electric Type A-H6 water cooled mercury lamp. Although small in physical size (about

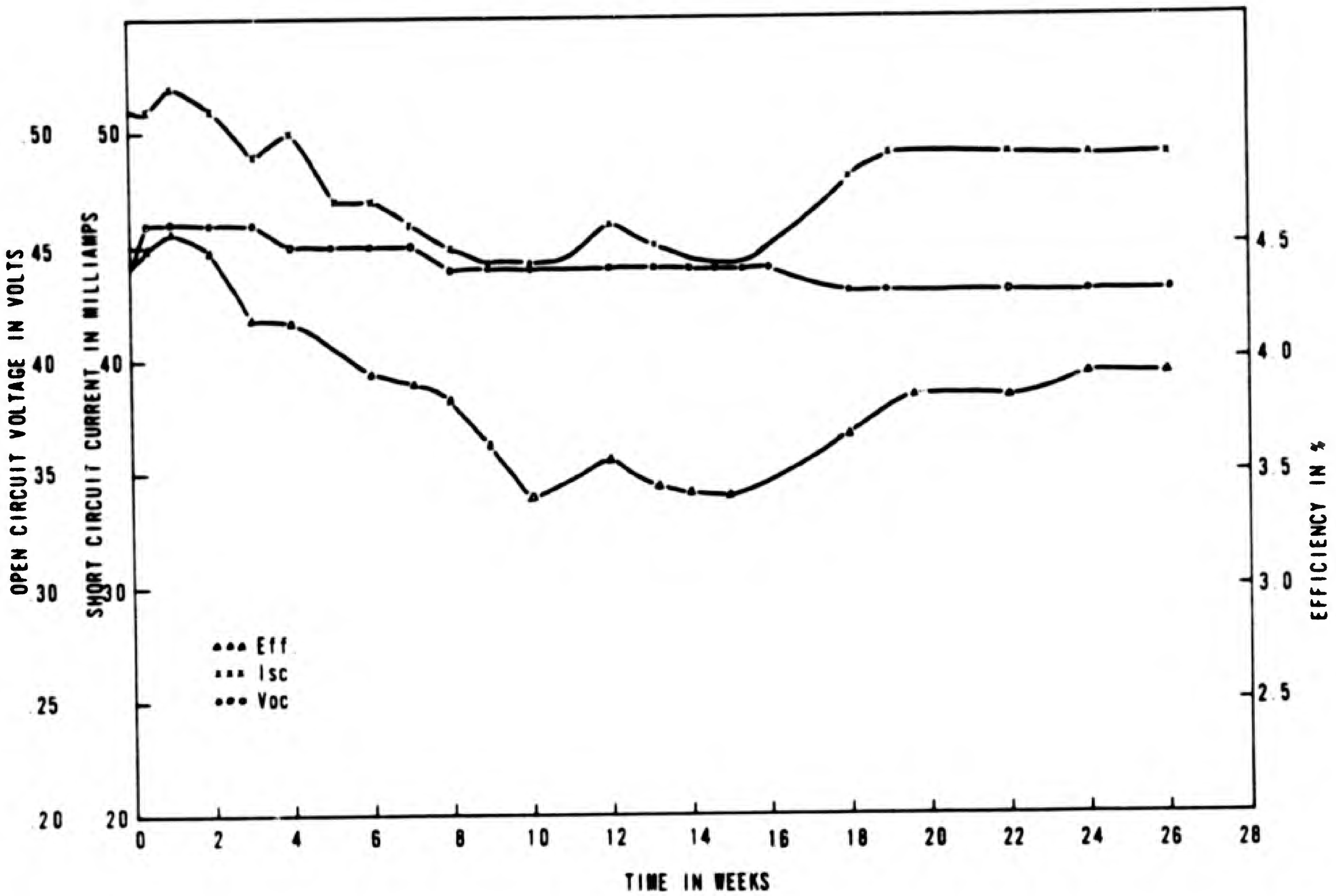


Fig. 2 Degradation Curve for Cell Z-21

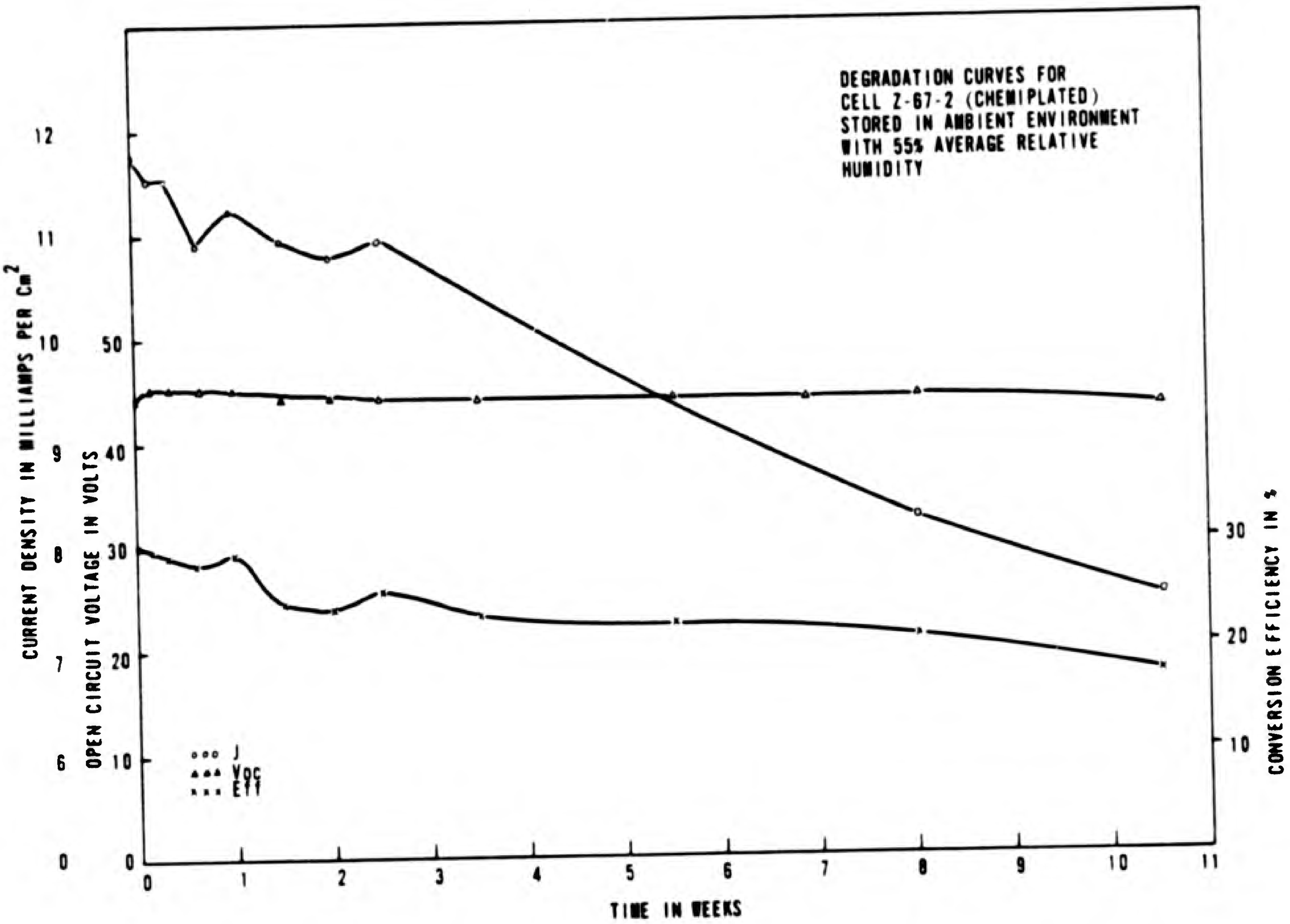


Fig. 3 Degradation Curve for Cell Z-67-2

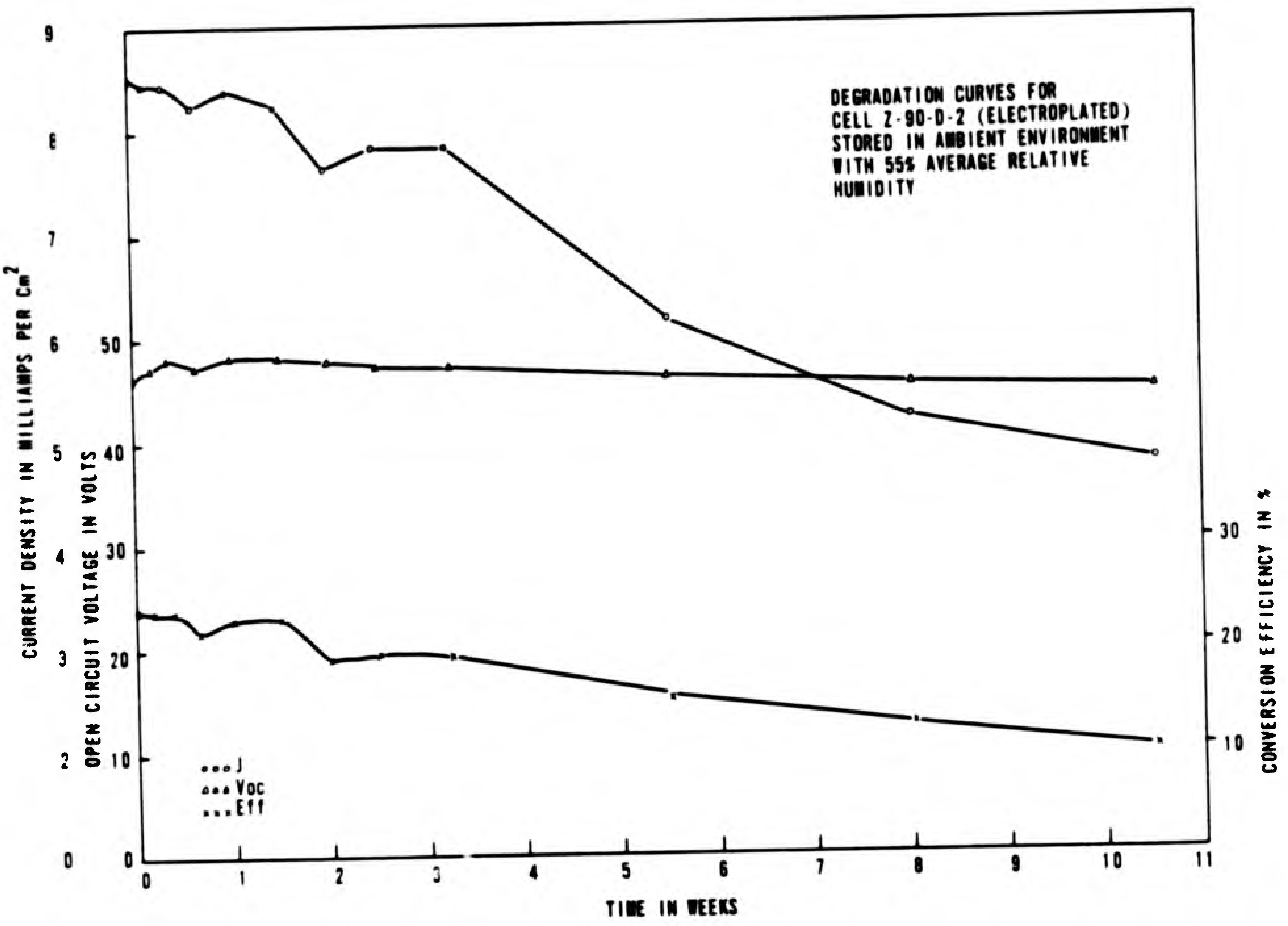


Fig. 4 Degradation Curve for Cell Z-90-D-2

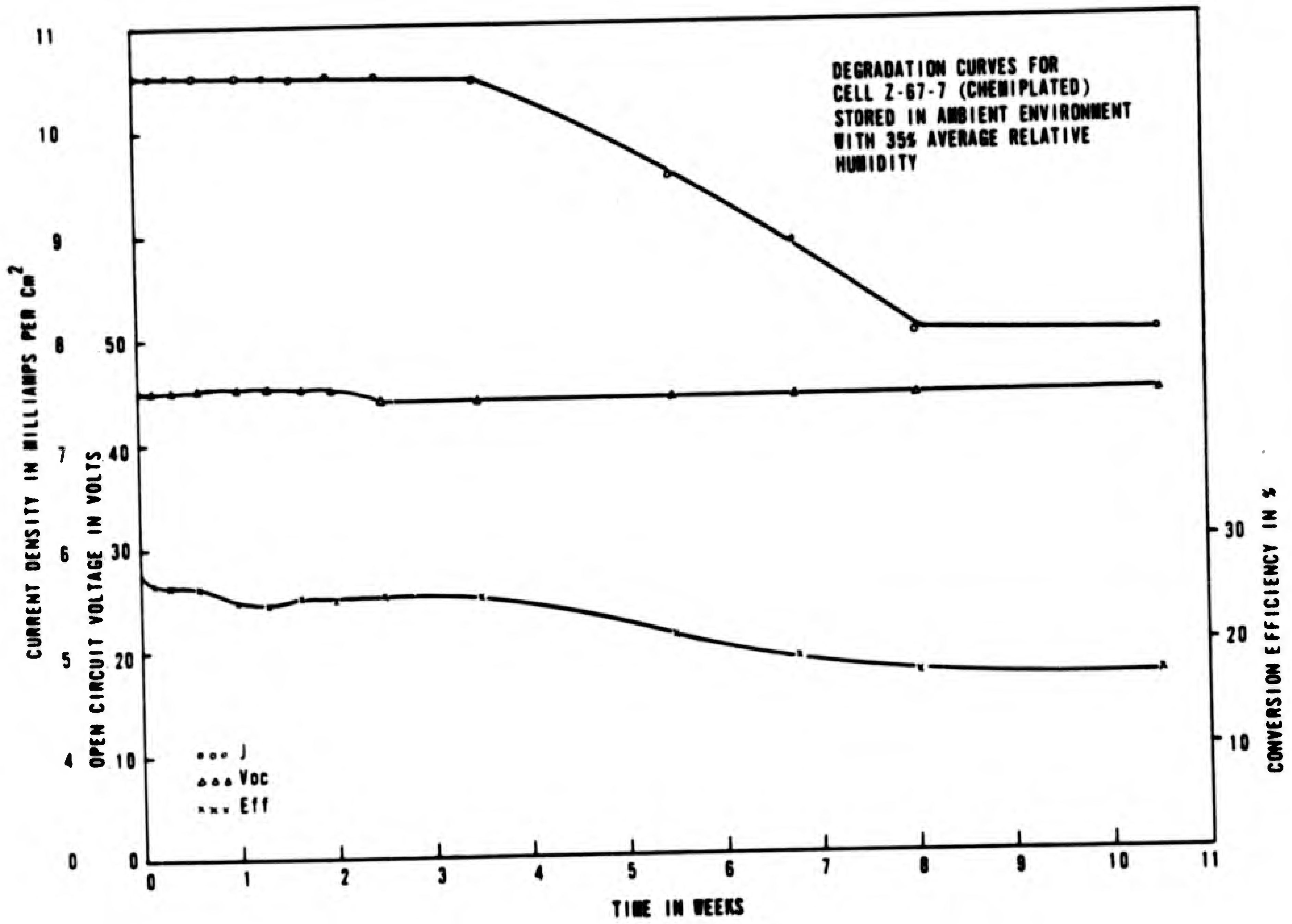


Fig. 5 Degradation Curve for Cell Z-67-7

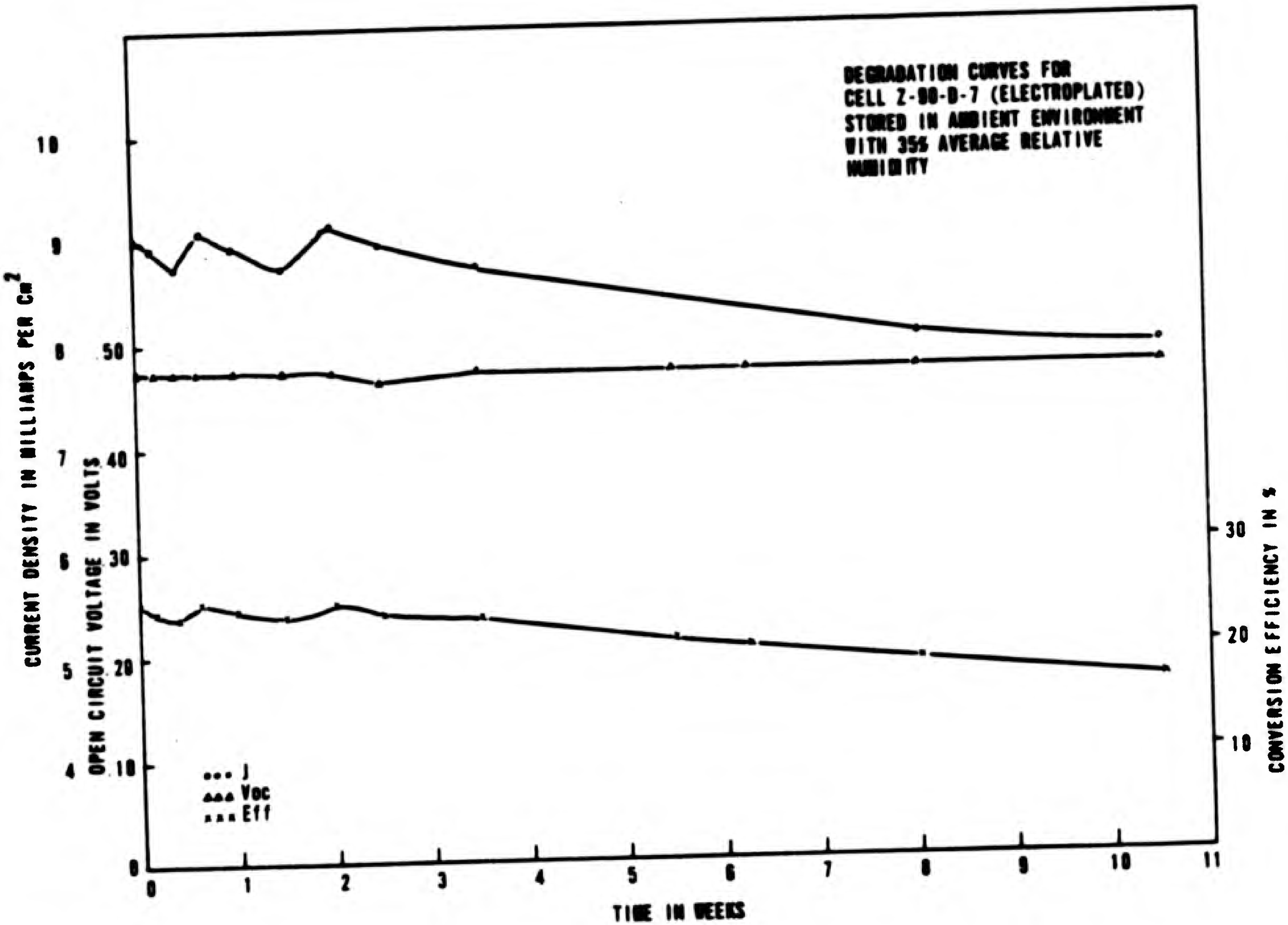


Fig. 6 Degradation Curve for Cell Z-90-D-7

1/16" diam. x 1" long), the lamp is rich in energy throughout the entire spectrum. About 17% of the watt input is radiated in the ultraviolet range of 3800 Å and below. The high wattage input of the lamp causes a considerable amount of heat to be generated during operation. In anticipation of this heat, an air blower was added to assist the normal water cooling of the lamp. For safety reasons, the lamp was also shielded to prevent damage to eyes and skin. It was also necessary to cool the fixture to which the sample materials were attached in order to alleviate any effects of heat from the high intensity radiation. This was accomplished by water cooling the fixture. The actual ultraviolet radiation was determined by measuring the watt output with an Eppley thermopile. A Corex A purple filter was placed over the thermopile opening to measure the output in the ultraviolet range of 3800 Å and below only. The distance from the lamp to the thermopile was set at 8.3 cm. This was the distance at which the samples were to be mounted on the cooled base plate. The output measured by the Eppley thermopile was 310 milliwatts per square centimeter. Space radiation in the same range is about 10 milliwatts/cm^2.(2) With this amplification of intensity as produced by the A-H6 lamp, the equivalent of one year ultraviolet radiation can be accomplished in about 280 hours. Several lamps were used during the accelerated exposure in order to insure adequate output during the entire test run. Figure 7 is a photograph of the pumping stand, vacuum chamber and ultraviolet source.

The first test run consisted of exposing thermoplastic films normally used in solar cell fabrication to an equivalent of one year exposure to ultraviolet radiation. Four samples consisting of films of Mylar (.001" thick), Nylon (.005" thick), H-film (.001" thick) and a Mylar-Nylon laminate were selected as the test films. During the test, the vacuum in the chamber varied from 5×10^{-6}mm Hg at the start to 1×10^{-6}mm Hg at the completion of the test run. During the change of the lamps, the samples were visually inspected. Considerable damage was noted for the Nylon and Mylar films with some darkening taking place in the Mylar-Nylon laminate but no apparent effect to the H-film. At the completion of the test period, the films were removed from the chamber and examined. The Mylar and Nylon films had decomposed so badly that any further tests could not be made. The Mylar-Nylon laminate as well as the H-film sample were tested for transmittance and reflectance and compared to curves of these samples made before the test. Figures 8 and 9 are the H-film transmittance and reflectance curves. Figures 10 and 11 are those of the Mylar-Nylon laminate. Observation of the curves show that the films are somewhat affected by ultraviolet radiation. This is especially true of the Mylar-Nylon laminate. The H-film was also affected but remains far superior to any materials tested.

A test shall also be performed on sample solar cells. These cells shall be of the electroplated and chemiplated types and shall be laminated in both Mylar-Nylon and H-film. Spectral Response curves will be made before and after the test. Temperature will also be monitored during the test run. This shall determine the lamination material for the one-half and one square foot arrays.

CONTACTING TECHNIQUES

The standard method for collecting current from the p-layer has been by means of a 70 line per inch gold grid. Contact to the p-layer by the gold grid is accomplished by pressure of the plastic film covering the thin

Fig. 7 Pumping Stand, Test Chamber and Ultraviolet Source

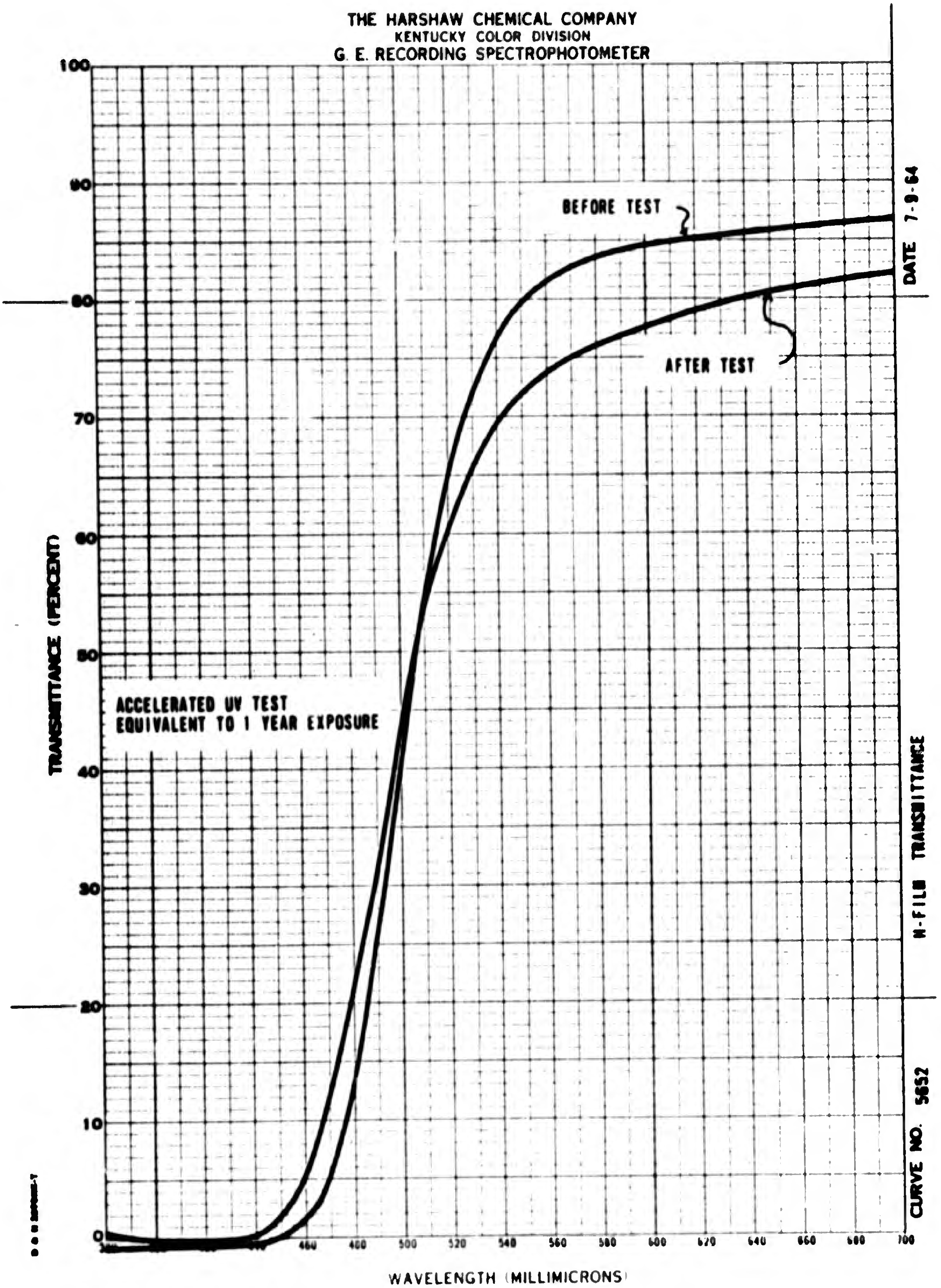


Fig. 8 Transmittance Curve of H-Film

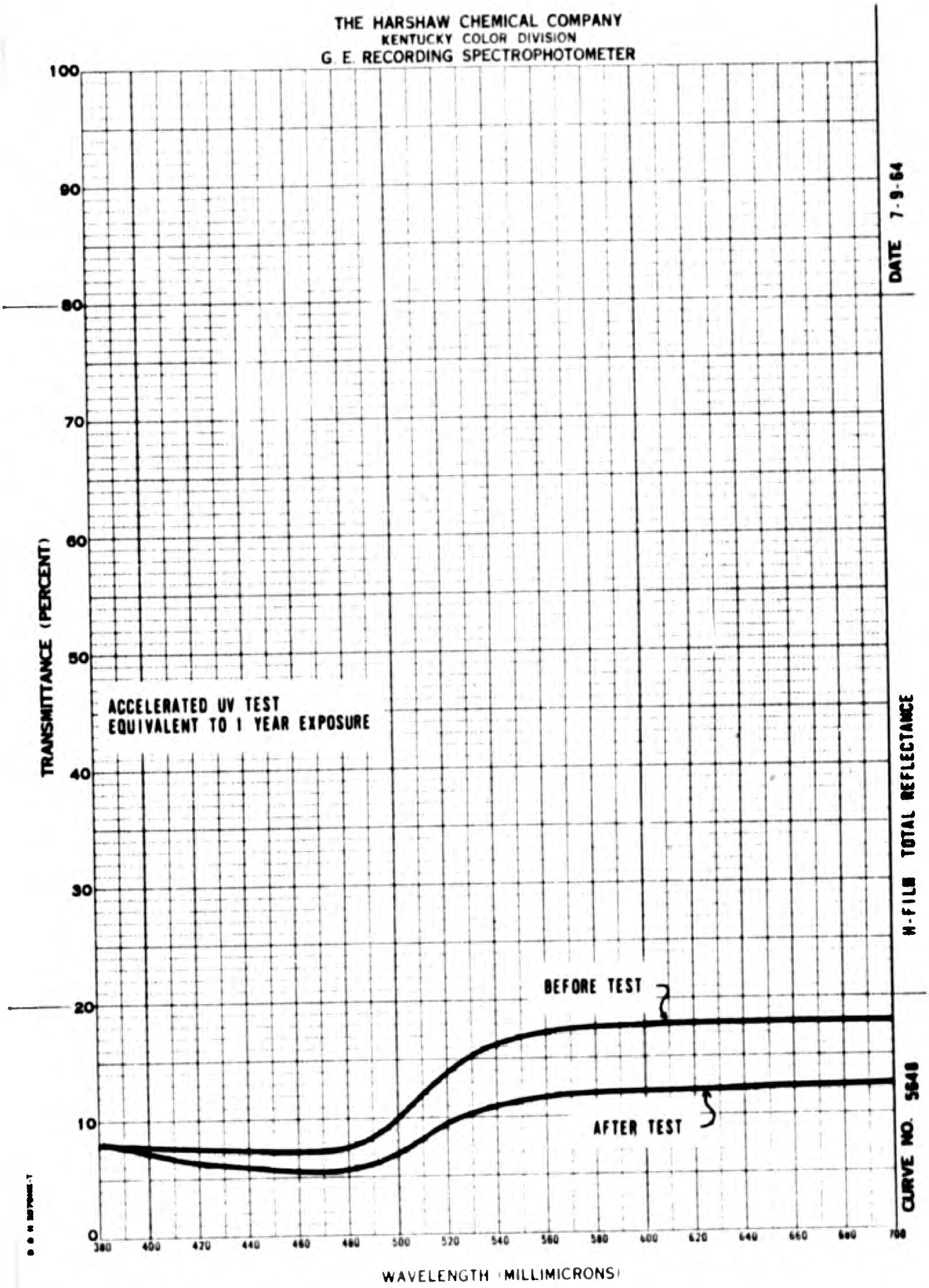


Fig. 9 Reflectance Curve for H-Film

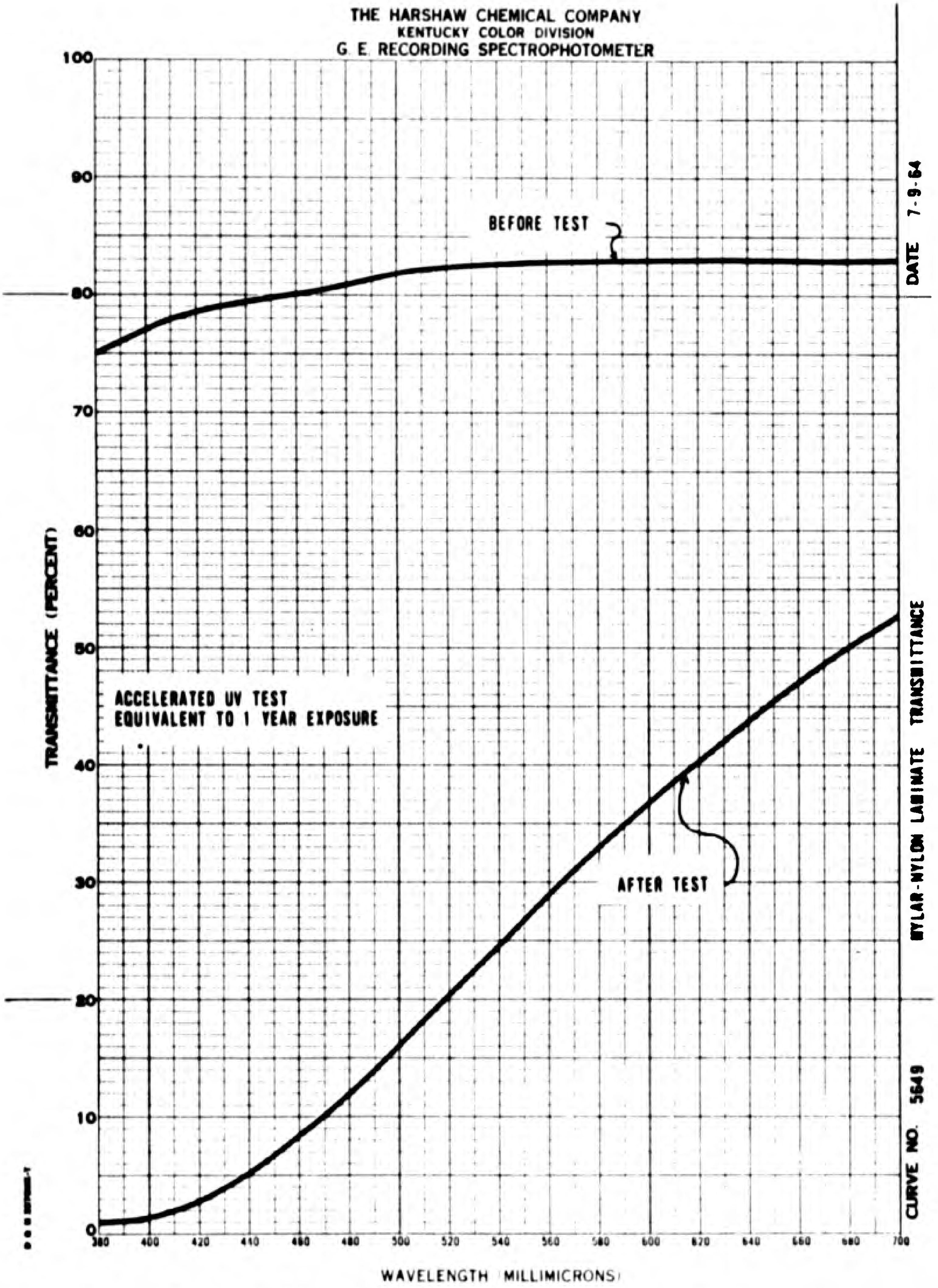


Fig. 10 Transmittance Curve of Mylar-Nylon Laminate

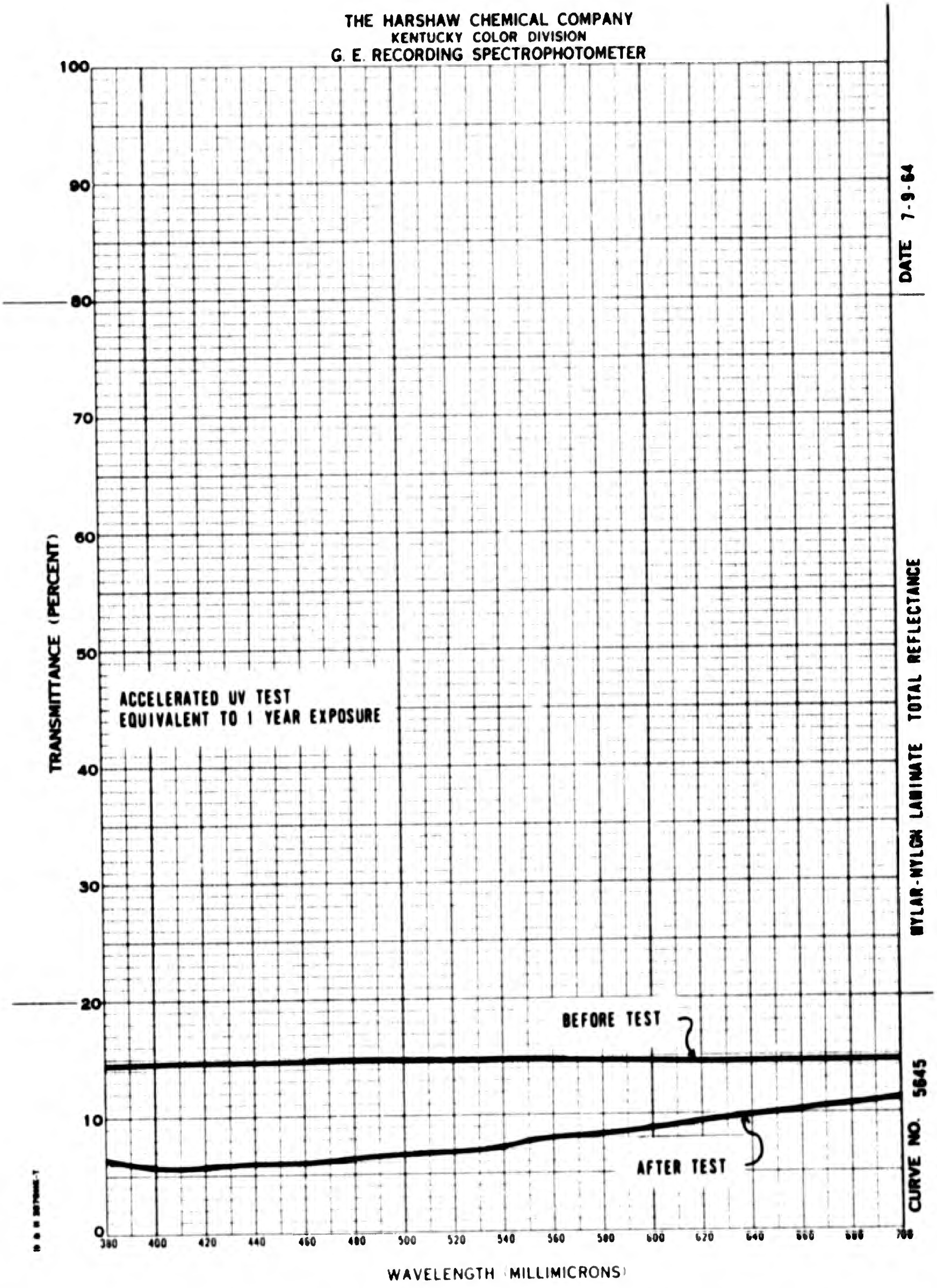


Fig. 11 Reflectance Curve of Mylar-Nylon Laminate

film cell. Naturally, the more intimate the contact, the less series resistance introduced in the finished cell. A number of other grid materials and shapes have been used as possible replacements, but none have been as efficient a collector as the electroformed gold.

Good results have been obtained by electroplating a gold grid directly to the surface of the solar cell. Both success and failure have been experienced in this process but the general trend is toward an improved collector grid. Cells with areas of about 9 in.^{2} have been made with efficiencies of about 2.5% to 3.0%. The limiting factor on these higher efficiency cells may have been due to the cells themselves rather than the electroplated grid. Several cells with electroplated grids have been tested by thermally cycling repeatedly between -70°C and +65°C several hundreds of times and have shown no loss in power.(3) Cells with electroformed grids eventually become erratic under the same conditions. At present, this type of grid formation is expected to replace the gold mesh now in use.

Sputtering techniques are also expected to produce satisfactory results. Equipment has been ordered for this method of application, but has not been received.

To help in the weight reduction of cells, extra thin (.0005") silver foil lead material is being tried. Results are not yet available. Comparison will be made to one mil silver and two mil nickel leads with regard to electrical characteristics.

RADIATION DAMAGE

As reported in the last Quarterly Report(4), a number of cells encapsulated in a variety of plastics were being exposed to a Cobalt-60 source in a vacuum environment. Official results have not been released as yet, but the verbal report has been quite favorable. Cells encapsulated in H-film were found to be better in efficiency than initially reported. The only damage noted was to the cells encapsulated in Tedlar. This particular plastic turned black after a short period of exposure time. Final results will be obtained from the U.S. Naval Research Laboratory at an early date.

More CdS thin film cells are to be exposed to proton radiation at NRL at energies of 1.8 and 3.0 Mev in the very near future.

Results will be reported as soon as available.

NEW CELL DESIGN

Emphasis on chemical milling techniques was the major item in new cell design.

Previous work areas included the evaporation onto H-film substrates to help reduce the weight of the thin film cell. The use of H-film as substrate material was actually quite successful. Efficiencies and watts per pound ratio were better than average. Four percent cell efficiencies and power to weight ratios of over 40 watts per pound were easily obtained on smaller area films. Wtih the advent of the chemical milling process, the weight advantage of H-film substrates has disappeared.

In the milling process, the film cell is fabricated in the usual manner and electroded. At this point, the substrate is milled, chemically, to a thickness of about 8 microns. As a result, the weight is greatly reduced and watts per pound ratios of greater than 40 can easily be achieved. This is possible even though the film cell efficiencies are only about 2.5%. Standardization will make it possible to incorporate this procedure in the cell fabrication of all array assemblies.

This method can also be used on titanium substrates which will in turn further reduce the overall weight. At present, the chemical milling procedure is being perfected for the molybdenum substrates.

Samples of chemically milled solar cells have been submitted to the Contract Monitor. The power to weight ratio of these samples were 41.3 and 36.2 watts per pound.

CELLS AND ARRAYS

Mechanical samples of both the one-half square foot and one square foot arrays have been assembled. The one-half square foot array is to be a nine cell symmetrical array that will have an active area of one-half square foot. With this arrangement, the array is capable of being laminated as one piece rather than two or three. In addition, the one square foot array will require only one seam for connection by impulse sealing methods. Previous square foot constructions required four edges to be sealed together. The principal feature of these arrays will be the close proximity between individual cells. The overall utilization factor of these arrays is expected to be greater than .70 as compared to .50 and .60 experienced previously. The individual cells that will be used in comprising the arrays should have watts per pound ratios greater than 30 with efficiencies around 3%.

Cells are being stockpiled now for both arrays. It is expected to have prepared both chemiplated and electroplated cells for array fabrication. With completion of the one-half square foot array, the simulated orbital temperature cycling test shall begin. All parts of the orbital chamber are now in operating condition.

PILOT LINE

The pilot line continues to operate for evaluation of film and cell quality. As stated in a previous section, considerable difficulty has been encountered in both film and cell fabrication. Although the average efficiency during this period continues to be about 2.0%, there have been cells fabricated that are acceptable for use in assembly of arrays. It is expected that the average efficiency will again return to a level of greater than 2.5% upon renovation of transistor washer.

PART II. RESEARCH

VAPOR DEPOSITION OF CuCl ON CdS

The previous quarterly report under this contract described initial experiments on the vapor deposition of CuCl to form thin films.(5) The possibilities of converting these thin layers of CuCl to semi-conducting Cu_2S were discussed. Application of the Cu_2S to a standard CdS evaporated film could form a highly abrupt p-n heterojunction if properly done. The resulting photovoltaic cell might provide further basic information on alternate techniques for fabrication. Certain theoretical ideas on the mechanism could also be checked as well as some experimental measurements. Emphasis was first placed on the controlled deposition of CuCl to give films in the range of 1000-3000 A. For these experiments, ordinary glass slides were utilized as substrates. A constant source temperature of 450°C was maintained. The substrate temperature was adjusted from 50 to 150°C. and the deposition times varied over 1 to 10 minutes. By suitable manipulation of the temperatures and times, a certain set of conditions was found to give films of the desired thickness. For each substrate temperature, the film thickness was checked by means of an interferometer attachment to a Reichert MeF microscope. A thin reflective layer of metallic Au or Ag was overdeposited on both the CuCl and the bare glass substrate to provide a measurement of CuCl thickness.

For several films an examination with x-rays showed that CuCl deposited with (111) planes of the cubic zinc blende structure parallel to the substrate. After treatment with H_2S gas, the transparent films of CuCl darkened to almost a metallic luster. A subsequent x-ray pattern of the product showed the elimination of the (111) orientation of CuCl and the appearance of several lines at other spacings. The complete assignment of these lines was not made because the intensities were very weak for the extremely thin layers. However, the data given by Mole and Hocart(6) on large polycrystalline grains was attributed to cubic and orthorhombic $Cu_{9.5}S_5$ phases at 25°C. Undoubtedly, the same phases are present in the thin films, but possibly with a certain preferred orientation.

From a knowledge of the evaporation variables of CuCl, it was possible to begin experiments relating to its deposition on CdS thin films. The latter were prepared in the usual manner with .002" Mo as a substrate. Several samples were obtained by subdividing a 3" x 3" or 6" x 6" CdS vapor deposited layer into 1" x 1" squares. The maximum temperature of these substrates was initially chosen as 150°C. Under the ambient conditions, no electrical or optical changes were noted in the CdS layers. The slight annealing involved could only serve to increase grain size but the short times were quite insignificant. Generally, the CuCl evaporations lasted from 1 to 5 minutes to deposit a thickness of not more than 3000 A. After the evaporations, each cell was tested in the pressure tester. A 70 lpi gold grid was applied to the top surface for a positive contact. At this position, some cells were found to be shorted but the majority gave an open circuit voltage of .1 to .3 volt, and a short circuit current of 1 to 10 milliamperes for a 4 cm^2 area.

Similar results had been achieved during previous experiments where CdS thin films were heated in CuCl powder at 150°C.

For the conversion of CuCl to $Cu_{9.5}S_5$, the films were placed in a closed container and dry H_2S gas was passed around the sample for 5 to 20 minutes. A darkening of the surface occurred and the cell appeared similar to those prepared by electroplating or chemiplating. Each cell was tested again in the pressure tester but no significant increase was found in either open circuit voltage or short circuit current. Brief heat treatments of 5 to 10 minutes were now given to the samples. This consisted of placing the samples in an oven regulated at 150°C with dry air as the atmosphere. After cooling the cells, all electrical tests were repeated. Now most of the measurements indicated no output. In only one case was there a significant increase in the open circuit voltage. For sample number 329 a value of .41 volt was reached. This is near to that observed for cells prepared by alternate techniques. A summary of all results is given in Table I.

Table I

ELECTRICAL DATA FOR CELLS PREPARED BY CuCl VACUUM EVAPORATED ON CdS

Cell Number	CuCl on CdS[a]		CuCl Converted to $Cu_{9.5}S_5$		$Cu_{9.5}S_5$ Heated to 150°C	
	Voc volts	Isc milliamps	Voc volts	Isc milliamps	Voc volts	Isc milliamps
329	0.3	8.0	0.2	4.0	0.4	2.5
330	0.2	2.0	0.2	3.0	No results	
331	Shorted		---	---	No results	
332	0.2	1.0	0.2	1.0	No results	
333	Diode		---	---	No results	
334	Diode		---	---	No results	
335	Diode		---	---	No results	
336	0.2	0.5	---	---	No results	
337	0.1	0.1	---	---	No results	

a) All cell areas were 4 cm^2

The poor results obtained on vacuum deposition of CuCl at 150°C were quite difficult to explain. Two possibilities were considered as direct causes. One was the known solid state reaction at 150°C between the compounds via the equation

$$(1) \quad 2CuCl + CdS \longrightarrow Cu_2S + CdCl_2$$

The presence of solid $CdCl_2$ could be troublesome by forming small insulated areas in either the CdS or the Cu_2S. The second alternative is simply a rapid diffusion of copper in the CdS to short out the cell. This diffusion seems to be assisted by the presence of Cl but no quantitative measurements have been made. In an attempt to minimize effects from reaction (1) and rapid diffusion, a temperature of 25°C was chosen for the CdS thin film substrates. A group of ten cells was prepared by vapor depositing not more than 3000 A of CuCl on the CdS. The samples were then tested electrically and all were found to be shorted. There was hardly any diffusion process which could account for these results. Ordinarily CuCl by itself does not have a high conductivity. Hsueh and Christy(7) give a value of $\sigma = 6.3 \times 10^6 \cdot \exp(-12300/T)(\text{ohm cm})^{-1}$ for a range of T from 400°K to 750°K. The addition of small amounts of $CdCl_2$ to CuCl does increase the conductivity but not to a large extent at 25°C. One other explanation would involve the oxidation of the CuCl to cupric compounds outside the vacuum chamber. The cupric compounds could act as dopants to give a nearly metallic like conductivity for the top layers. Such a process is known to occur in thin films of Cu_2S doped with CuS. Cracks and grain boundaries in these layers may then cause leakage and shorts. Further experiments have to be performed particularly with the CuCl converted to $Cu_{9.5}S_5$.

BASIC BARRIER STUDIES - OPTICAL

Rather complete optical measurements on the chemiplated barrier were published in the second quarterly report. These measurements provided strong evidence for the presence of Cu_2S or Cu_9S_5 in the chemiplated barrier as applied to single crystal CdS. Subsequent measurements on electroplated barriers showed relatively low reflectivity. This result was interpreted as indicating an absence of Cu_xS compounds, or at least of Cu_2S. This conclusion was based on knowledge of the refractive index of Cu_2S, such an index being incompatible with the observed low reflectivity. It is clear that CuS has a much lower refractive index than Cu_2S and thus can account for the observed reflectivity of the electroplated barrier on single crystal CdS. It appears that the optical properties of both the chemiplated and the electroplated barrier can be explained by assuming a preponderance of Cu_2S and CuS in the respective barriers. Further, the Cu_2S in the chemiplated case is partially converted to CuS by heat treatment in an oxidizing atmosphere.

The above conclusions are based on comparison of observed spectra on the two types of barrier with the data of Eisenmann(8). Figure 12 is reproduced from the second quarterly report, and shows the similarity of the chemiplated barrier's absorption spectra to that of Cu_9S_5 as determined by Eisenmann(8). Figure 13 shows the reflectivity of an electroplated barrier in comparison with Eisenmann's data on CuS. The differences in shape are due to interference effects as well as to the possible incomplete coverage of CdS by the electroplated barrier. The overall agreement is quite satisfactory for establishing the optical nature of the barriers.

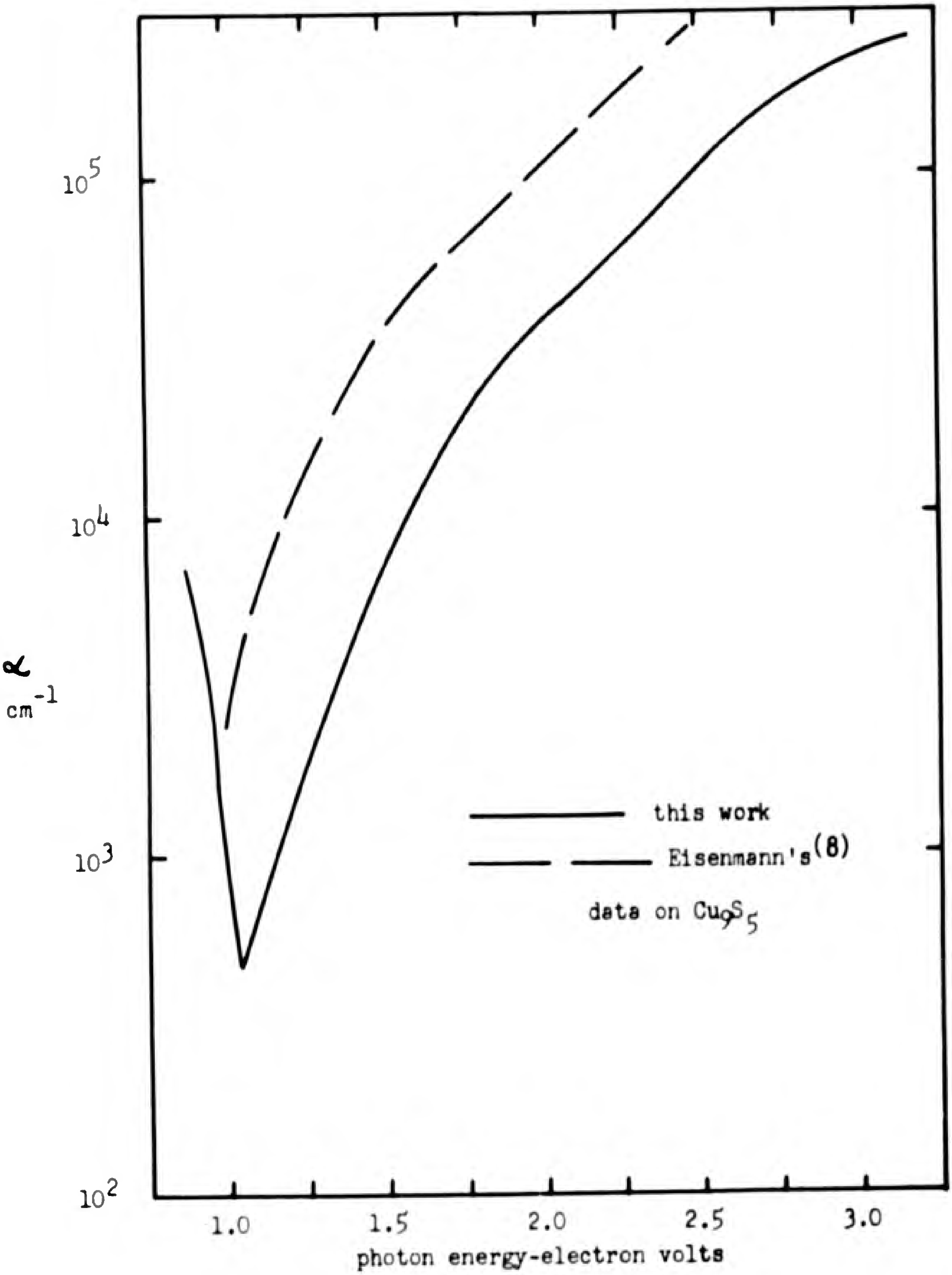


FIGURE 12

Absorption Coefficient vs Photon Energy for the Chemiplated Barrier

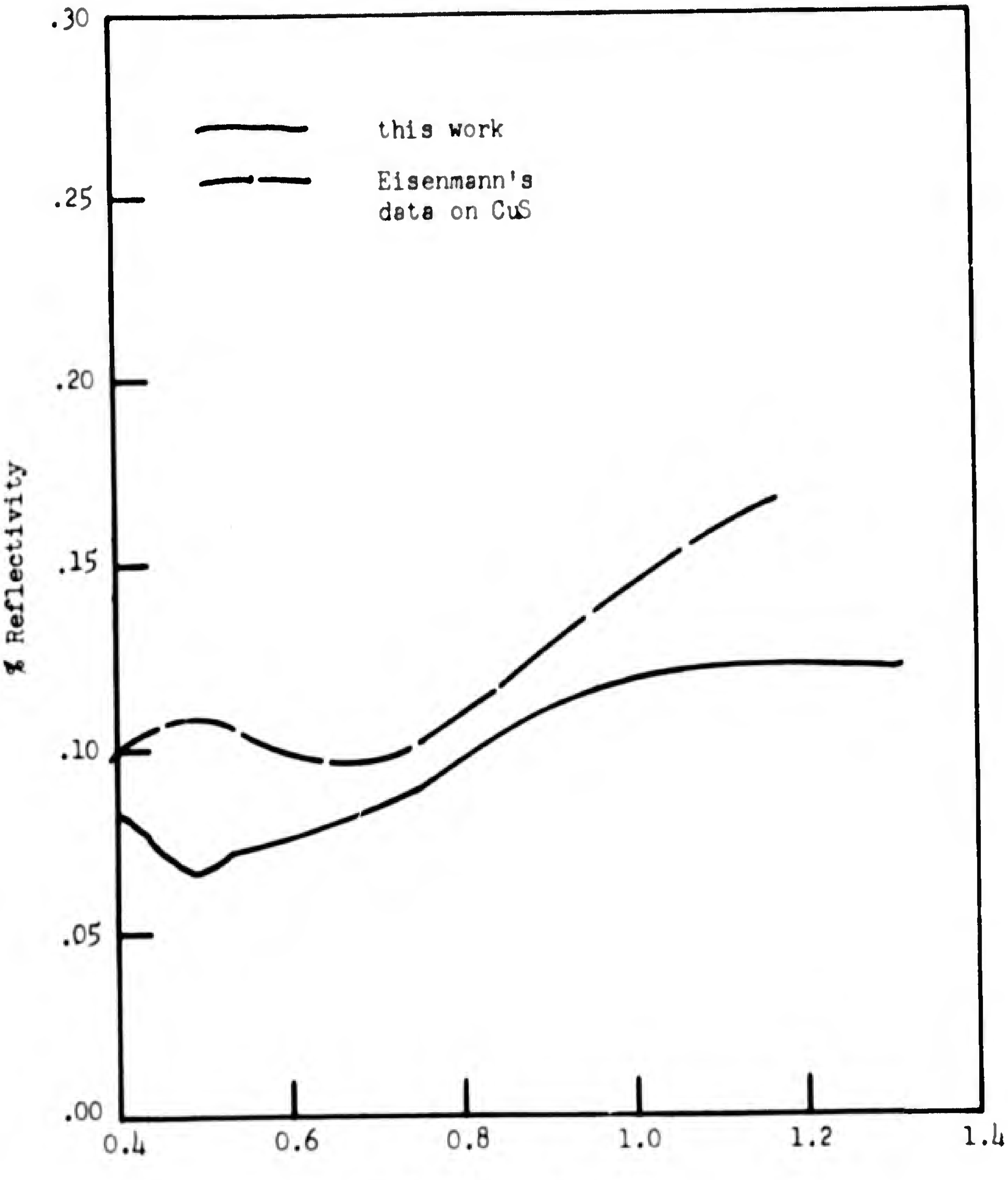


Figure 13

Reflectivity vs. Wavelength for the Electroplated Barrier

INHIBITION OF EFFICIENCY DECAY

Tests have been performed to determine the effectiveness of thin films of SiO in protecting the CdS cell from water vapor. Electroplated barrier cells were contacted with an evaporated silver grid electrode. Five pairs of cells were prepared with evaporated SiO coatings.

1. Cells coated with vacuum evaporated SiO, 300 Å thick
2. Cells coated with vacuum evaporated SiO, 1000 Å thick
3. Cells coated with vacuum evaporated SiO, 3000 Å thick
4. Cells coated with vacuum evaporated SiO, 10000 Å thick
5. Cells coated with sputtered pyrex, 10000 Å thick

One of each pair was placed in a closed container over liquid water at room temperature and the other placed in a desiccator. The cells were removed from the container for short periods of time for testing under RFL-2 tungsten simulated sunlight.

The behavior of measured short circuit current as a function of time is shown in Figures 14 and 15. For comparison, the same data for a cell encapsulated in Mylar and Nylon is shown. The cells in the desiccator showed no change in short circuit current over the period of the test.

It is clear that the SiO affords good protection from water vapor and that layers 300 and 1000 Å thick seem to be sufficient if not optimum. Since these layers were deposited onto room temperature substrates, it is quite possible that 10,000 Å and thicker layers are mechanically unstable and subject to peeling. This can explain the poor behavior of the thicker layers.

After approximately 430 hours exposure to water vapor, the cells were returned to a desiccator. No further change or recovery was observed, indicating an irreversible process.

The same type of test was performed using painted-on or sprayed-on layers of Krylon and H-film varnish. The behavior of these cells was similar to those in Mylar and Nylon plastic; that is, they were for practical purposes lost after 24 hours exposure.

From these data, it appears that SiO layers will protect the cells from water vapor over reasonable periods of time, certainly more than any plastic covering. Further work will be done on the investigation of other inorganic films such as MgF_2, CaF_2, ZnF_2.

THEORETICAL STUDIES

Attempts have been made to understand the CdS photovoltaic cell by means of the heterojunction model. The cell is assumed to be composed of

Fig. 14

Short Circuit Current as a Function of Time
for coated cells

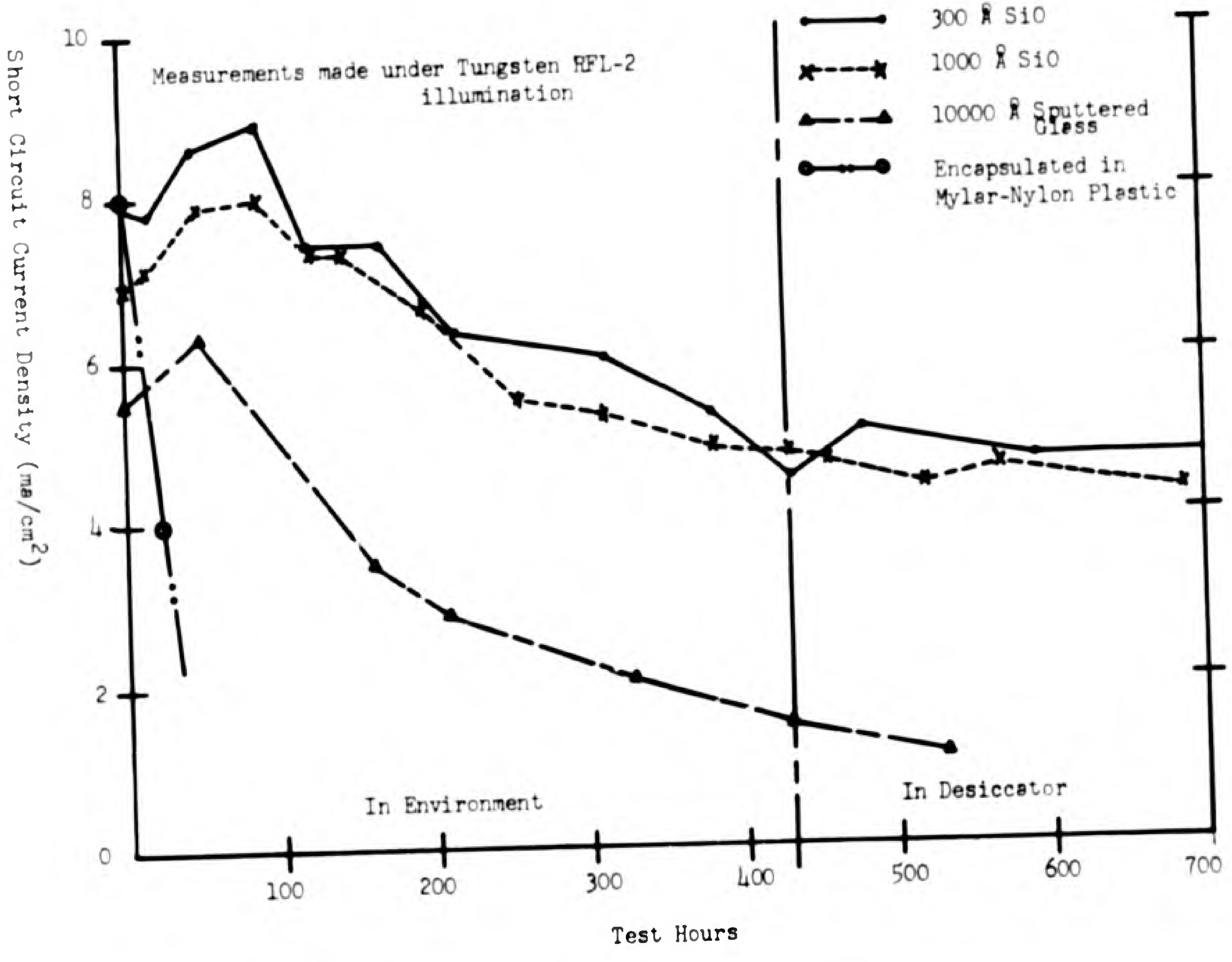
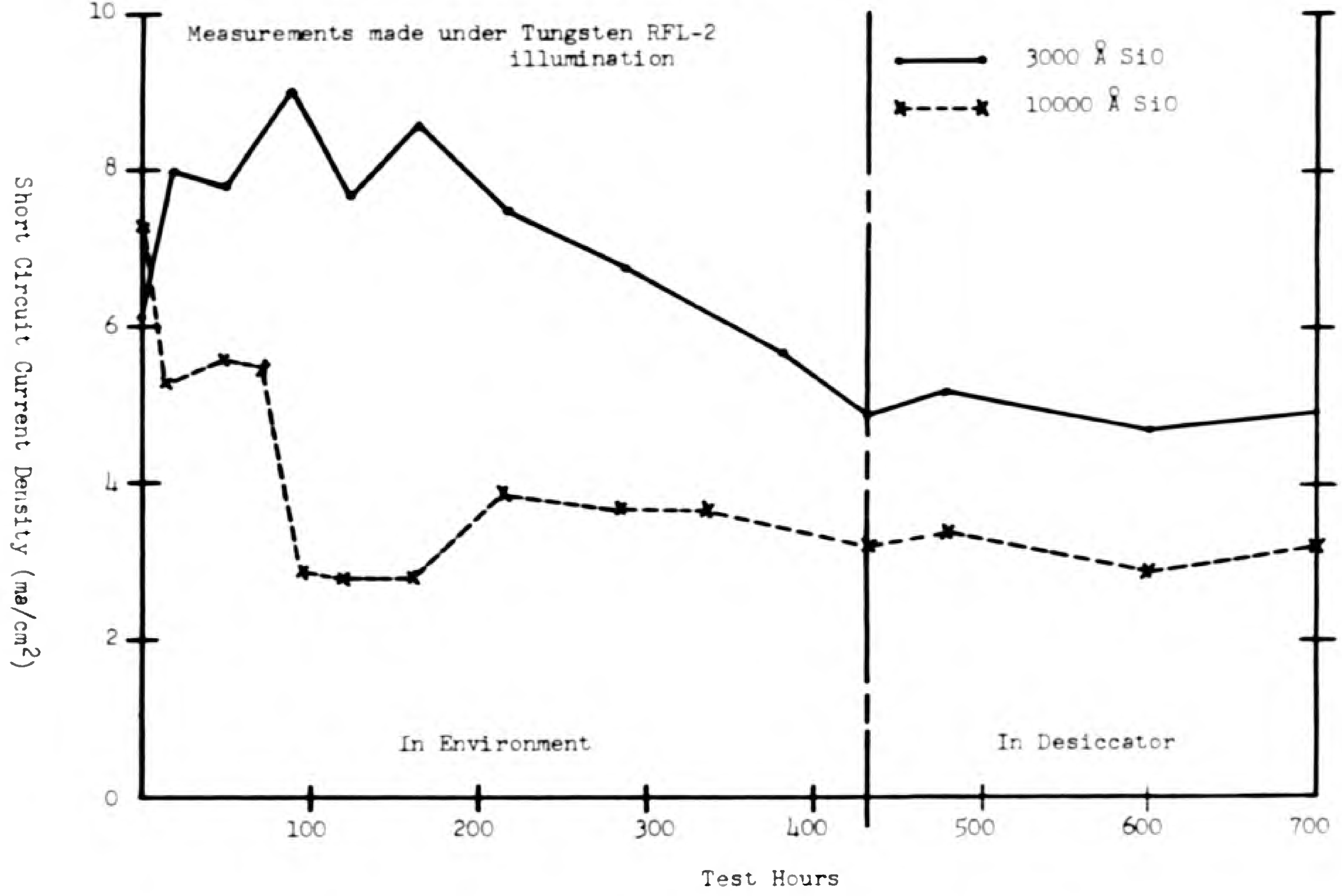


Fig. 15

Short Circuit Current as a Function of Time
for coated cells



three layers: the bulk n-type CdS, a p-type semi-conducting material (band gap 1 eV), and a p-type semiconductor with band gap approximately 2.4 eV. The following simple presentation will show the heart of the problem. If one assumes that for each consecutive pair of junctions, the ordinary photovoltaic I-V characteristics hold, then one obtains the following equations:

$$I_1 = I_{01}(e^{qV_1/kT} - 1) - I_{L1}$$

$$I_2 = -I_{02}(e^{qV_2/kT} - 1) + I_{L2}$$

$$I = I_1 = I_2$$

$$V = V_1 - V_2$$

where V is the applied voltage which will be divided into two parts for the front and back junctions, and I_{L1} and I_{L2} are the currents generated by light for the junctions. These equations can be readily solved for I and V to give:

$$(I + I_{L1} + I_{01})/(I_{L2} + I_{02} - I) = (I_{01}/I_{02})e^{qV/kT}$$

This shows the saturation currents in both directions of voltages, and the linear response of short circuit current with light intensity. However, this does not reflect the observed behavior of the CdS photovoltaic cell, probably because the importance of the middle layer is completely neglected. Therefore, it is premature to be conclusive about this model and a more refined treatment will be continued in the following months from the viewpoint of the heterojunction model.

WORK PLANNED FOR NEXT QUARTER

Ultraviolet studies on sample cells will have been completed. Fabrication of the one-half and one square foot arrays shall be finished. Orbital testing of the one-half square foot shall also be completed.

Thin films of CdS will be prepared at high substrate temperatures. Doping agents will be used for increasing the room temperature conductivity while attempting to increase grain size and perfection.

Other inorganic compounds will be deposited on completed photovoltaic cells to inhibit degradation by water vapor.

Theoretical study of the heterojunction model of operation will continue.

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