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THIRD QUARTERLY REPORT

ON

DEVELOPMENT OF OPTICAL COATINGS

FOR

CdS THIN FILM SOLAR CELLS

BY

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Prepared For

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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THE HARSHAW CHEMICAL CO.

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Technical Management
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Cleveland, Ohio
Space Power Systems Division
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FOREWORD

This report was prepared by The Harshaw Chemical Company, Crystal-Solid State Division under Contract NAS 3-6464 for the NASA Lewis Research Center. Dr. A. E. Potter and Mr. C. Swartz have served as Technical Advisor and Project Manager respectively.

The Harshaw Solid State Laboratory is directed by Dr. J. M. McKenzie, Technical Director. Project direction is provided by Mr. E. R. Hill with Mr. J. C. Schaefer serving as Project Supervisor. The following Harshaw Chemical Company personnel have contributed to this program: R. W. Olmsted, R. J. Humrick and A. Hartzler.

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CdS THIN FILM SOLAR CELLS

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SUMMARY

Suitable glass coatings have been sputtered on CdS solar cell surfaces. Addition of oxygen to the sputtering gases has produced stable films of low reflectance. Efforts are being made to increase the rate of sputtering. A four electrode target electroded on the rear surface of the glass target indicates increased rates.

Measurements of spectral reflectance were made on a number of samples, including a silicone primer paint.

Apparatus has been assembled for measurement of emittance at solar irradiation power levels. Emittances have been determined for bare cells and a number of other surfaces.

INTRODUCTION

The purpose of this program is to develop and apply optical coatings to CdS solar cells for the purpose of increasing the power conversion efficiency. It is desired to maximize the amount of light entering the cell in the region of the spectrum where the cell is sensitive, reject all others, and reduce the operating temperature of the cell in outer space. These conditions are not all independent since a coating which reflects strongly in the infrared will also reduce the emissivity in the region of maximum cell reradiation. The objectives stated can be reached by developing a coating with a high transmission to wave lengths less than about 1 micron, has a refractive index of about 1.2 to 1.3 in this same range and absorbs relatively strongly (about 10^{-3} to 10^{-4} cm^{-1}) in the

range of 5 to 30 microns. These properties are satisfied by ordinary glass and consequently has been the first material to be investigated to any extent.

Other obvious properties to be desired are compatibility with the device, mechanical and chemical stability, and resistance to environmental effects. In addition, it is desirable to have the coating seal the cell from atmospheric water vapor.

COATING DEPOSITION

The primary purpose of the deposition work during this past quarter was the development of a method of applying the coating at a higher rate. The higher rate was necessary to produce a coating of sufficient thickness within a practical period of time.

Earlier in the contract it had been observed that use of the R.F. electrode in contact with the dielectric target face resulted in "hot spots." These were white-hot pinpoints which quickly heated the surrounding pyrex to a red heat and, in some cases, caused the glass to bubble. Their small size suggested that the hot spots formed at the points of mechanical contact between the electrode and the pyrex. It had also been found that sputtering could be achieved with the electrode spaced 1-2mm behind the dielectric. Refer to the fourth and fifth entries of Table I. It was thought, however, that placing the electrode in intimate contact with the target dielectric over a large area would result in better transfer of power to the dielectric. For this purpose, conductive silver-glass frit was fired onto the back of a four inch diameter pyrex disc. When this target was used, a yellow color, indicative of sodium, appeared on the target surface and in the plasma column at a relatively low net RF power. A "hot spot" did, however, develop. This hot spot was cooler and did not correspond to a point of contact between the silver layer and the back-up electrode. It was apparently a result of an inhomogeneity in the glass and the negative temperature coefficient of the glass electrical resistivity. The pyrex cracked in this area.

A smaller (two inch diameter) disc of pyrex was coated with the silver. Effective power transfer was again achieved with this target, but there appeared to be less tendency for hot spots to develop. A target of this approximate size is compatible with the square four-target array.

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Installation of the four-target array has brought about a number of mechanical problems. None of these are of concern.

As might be expected, the use of a thinner dielectric contributes to a higher deposition rate. This effect was observed experimentally during this past quarter.

A secondary effort, during this past quarter, was directed toward increasing the mechanical stability of the coating. This was necessary because certain earlier coatings spontaneously peeled or blistered from the cells on which they were deposited. Experiments have been conducted which indicate that the addition of oxygen to the sputtering atmosphere permits the formation of coatings with reduced stress. The use of ambient laboratory air gave rise to coatings of unsatisfactory clarity and color. The deposition rate was very low when oxygen alone was used. The atmosphere showing the most promising results was a mixture of argon and oxygen. Examples of this combination were cells produced with 60% of Ar, 40% of O_2 and 80% of Ar, 20% of O_2 respectively. The cell produced with only 20% of O_2 showed a slight tendency to peel in humid air. Table I is a listing of representative runs made throughout the quarter.

The effect of pure oxygen in reducing the sputtering rate is seen. Also, the relatively high rate produced by the silvered target is seen in that a normal rate is observed for a rather low input power.

REFLECTANCE AND EMITTANCE MEASUREMENTS

Spectral reflectance measurements provide an easy means of measuring emittance when the reflectance spectrum is simple in structure. However, the presence of absorption and reflection bands in the infrared complicate calculation of emittance at low temperatures. In this case, it is simpler to assemble a radiator from the material to be studied and measure its temperature at a known power dissipation. An apparatus has been assembled to do this, shown schematically in Figures 5 and 6.

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TABLE I

Date	Ion Gauge (μHg)	Anode Potential (Volts)	Anode Current (Amps)	Net RF Power (Watts)	Substrate Temperature (°C)	Deposition Rate (Å/hr)	Remarks
6-8 to 6-10	0.9	88	1.0	360	210	.12	Air
6-14 to 6-16	0.5	80	1.8	380	180	.24	Argon, Mo & Al sheets
6-17	1.0	95	.25	350	130	.05	Oxygen
6-21 to 6-24	1.0	85	2.0	360	150	.15	60% Ar, 40% O_2
6-29 to 7-8	0.6	75	2.0	380	150	.13	80% Ar, 20% O_2
7-16	0.6	100	1.0	390	170	.10	Argon
7-19	0.65	85	.8	390	180	.23	Argon, Crystallization Dish
7-27	0.65	67	.3	100	94	.13	Argon, Silvered Crystallization Dish

A vacuum stand with a blackened 14 inch glass bell jar provides an iso-thermal room temperature enclosure. A thin, flat heater coated with the material in question is suspended in this space. The heater is made from a 1-1/2 x 1-1/2 x 1/16 inch flat coil of #36 copper wire with a room temperature resistance of about 50 ohms. The sample material is mounted to both faces of the heater and the temperature of the heater determined from the resistance of the copper coil. The thermal equation for this system is:

$$\frac{dT}{dt} = C \left[P + P_1 - P_2 - e A \sigma T^4 \right]$$

where:

P   =   heater power

P_1 =   power contributed to the sample by radiation from the enclosure and by sample radiation reflected back to the sample.

P_2 =   power lost by conduction and convection.

T   =   sample surface temperature.

C   =   heat capacity of the sample.

A   =   surface area of the sample.

σ =   Stefan-Boltzmann constant.

e   =   total emittance of the sample.

At a steady-state condition the thermal equation reduces to:

$$0 = P + P_1 - P_2 - eA \sigma T^4$$

The quantity P_1 can also be minimized by keeping the walls of the chamber at a significantly lower temperature than the sample surface and by blackening the chamber walls to eliminate, or at least greatly reduce, the amount of reflection from the walls. This will reduce P_1 from

$$P_1 = Aa \sigma T_o^4 + A \sigma T^4 \; Re \left[\frac{1}{1 - (1-e)R} \right]$$

to:

$$P_1 = Aa \sigma T_o^4$$

P_2 is made small by evacuating the chamber and by using light lead wires.

A = surface area of sample

a = absorptance of sample

T_O = wall temperature

R = wall reflectance

We then arrive at the relation:

$$0 = P + Aa\sigma T_O^4 - eA\sigma T^4$$

Measuring power and temperature at three points allows the determination of A, a, and e from three simultaneous equations. Since we are primarily interested in temperatures under solar irradiation, emittance was determined for power dissipation in the neighborhood of 70 mw/cm^2. Table II shows the steady state power and temperatures for various material tested. Figure I is the spectral reflectance of polished aluminum, showing the emittance to be 0.05 at a maximum, agreeing quite well with the measured value of 0.02. The bare CdS cell emittance was measured at about 0.2. Comparing Figures 2 and 3, the measured reflectance is very close to 80%, making the emittance about 0.2. Finally, the emittance of the silicone primer, GE55-4044 was measured to be 0.26. Figure 4 is the reflectance spectrum of this primer on polished aluminum. Integration and averaging of this curve gave an average reflectance of 0.58, or an emittance of 0.42. The same primer on a cell gave a measured emittance of 0.22.

FUTURE WORK

It is expected that the four target array will soon be operating more effectively, producing more uniform coatings at a higher deposition rate.

The relation of electron emission rate from the sputtering unit's hot cathode to the deposition rate will be checked. Possibly, a better electron emitter can raise deposition rate in two ways. The first way would be by

TABLE II

Material	Power mw/cm^2	Sample Surface Temperature ^{o}K	Emittance (Calc.)
Alumina	62	388°	.73
Alumina w/cover glass	50	247°	.83
Aluminum Sheet	13	533°	.02
Aluminum Sheet coated w/GE silicone primer GE-SS-4044	26	400°	.26
Aluminum Sheet covered w/flat black paint	15	380°	.20
CdS cell	27	464°	.18
CdS cell coated w/silicone primer	17	415°	.22

increasing the ion density in the plasma providing more power concentrations in the target. The second way would be the permitting of the use of a lower gas pressure, thereby, reducing the scattering of the material particles.
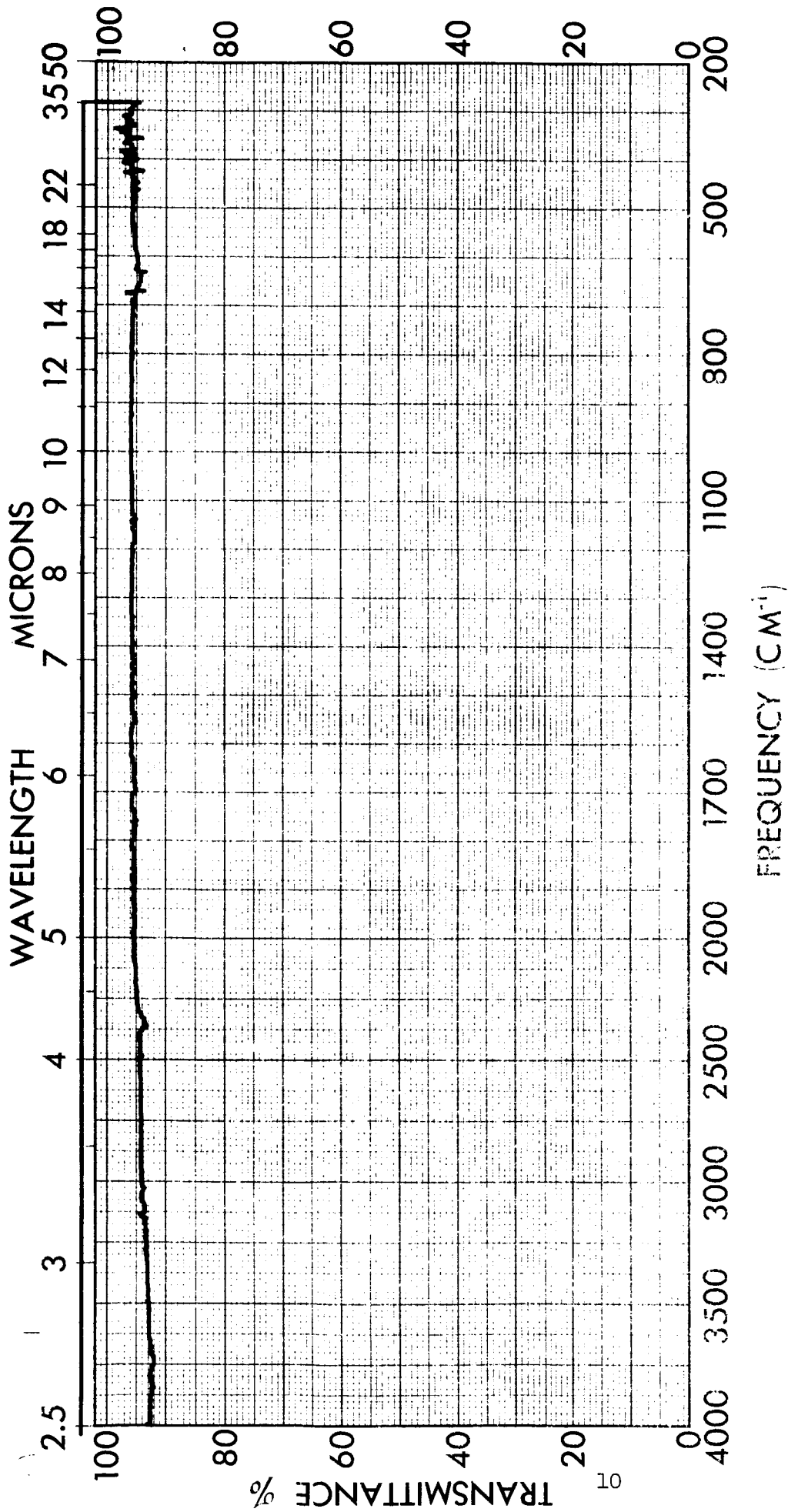
The substrate cooler will be used to avoid temperature degradation of the cells during deposition.

Alternate target materials now on hand will be evaluated.

Sample cells will be sent to NASA periodically.

Measurements of emittance and reflectance on samples will continue, specifically on coated CdS cells.

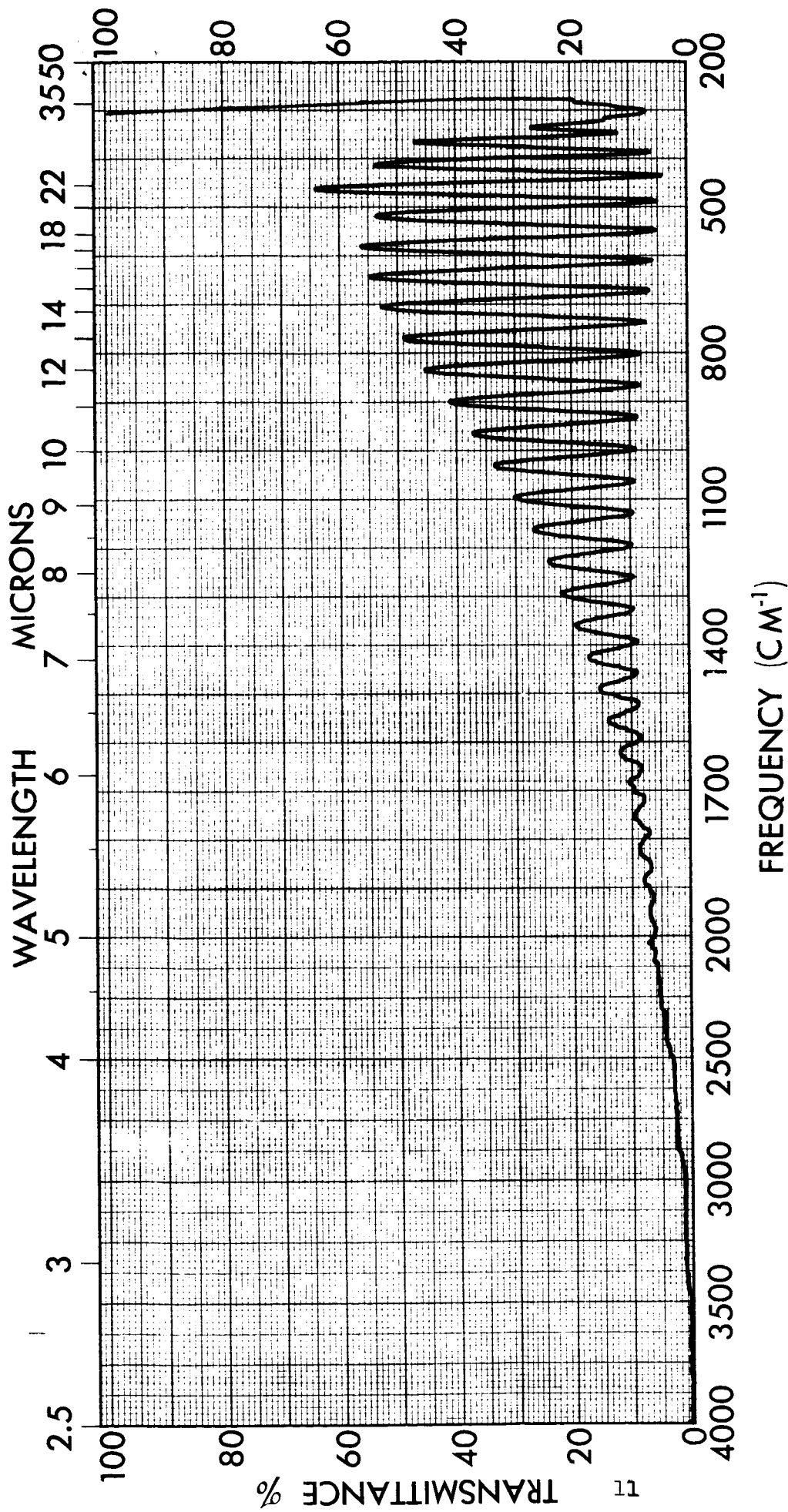Operating CdS cells will be coated and tested.

Figure 1. Specular Reflectance Spectrum of Polished Aluminum

Spectrum No. G-1753

Sample: Aluminum (on alumina Sheet)
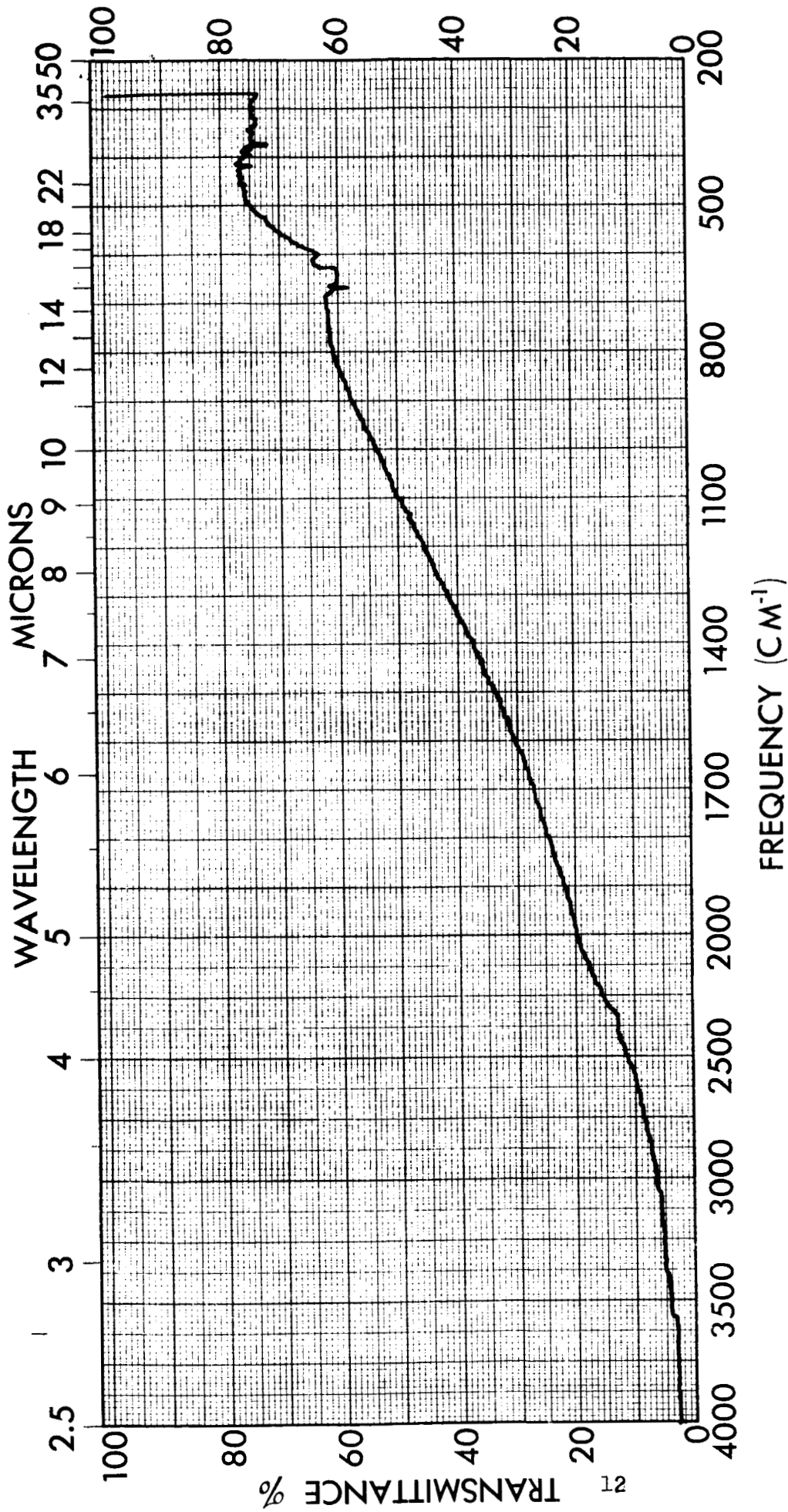
Origin: AN 65287

Phase: Solid

Date: 8-19-65

Remarks: Specular Reflectance Spectrum

Figure 2. Specular Reflectance Spectrum of CdS Cell

Spectrum No. G-1622   Phase: Solid

Sample: CdS Cell (S-55 III)   Date: 7-6-65

Remarks: Specular Reflectance Spectrum

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Spectrum No. G-1619   Phase: Solid

Sample: CdS Cell (+Al, S-55I)   Date: 7-6-65

                        Remarks: Specular Reflectance Spectrum

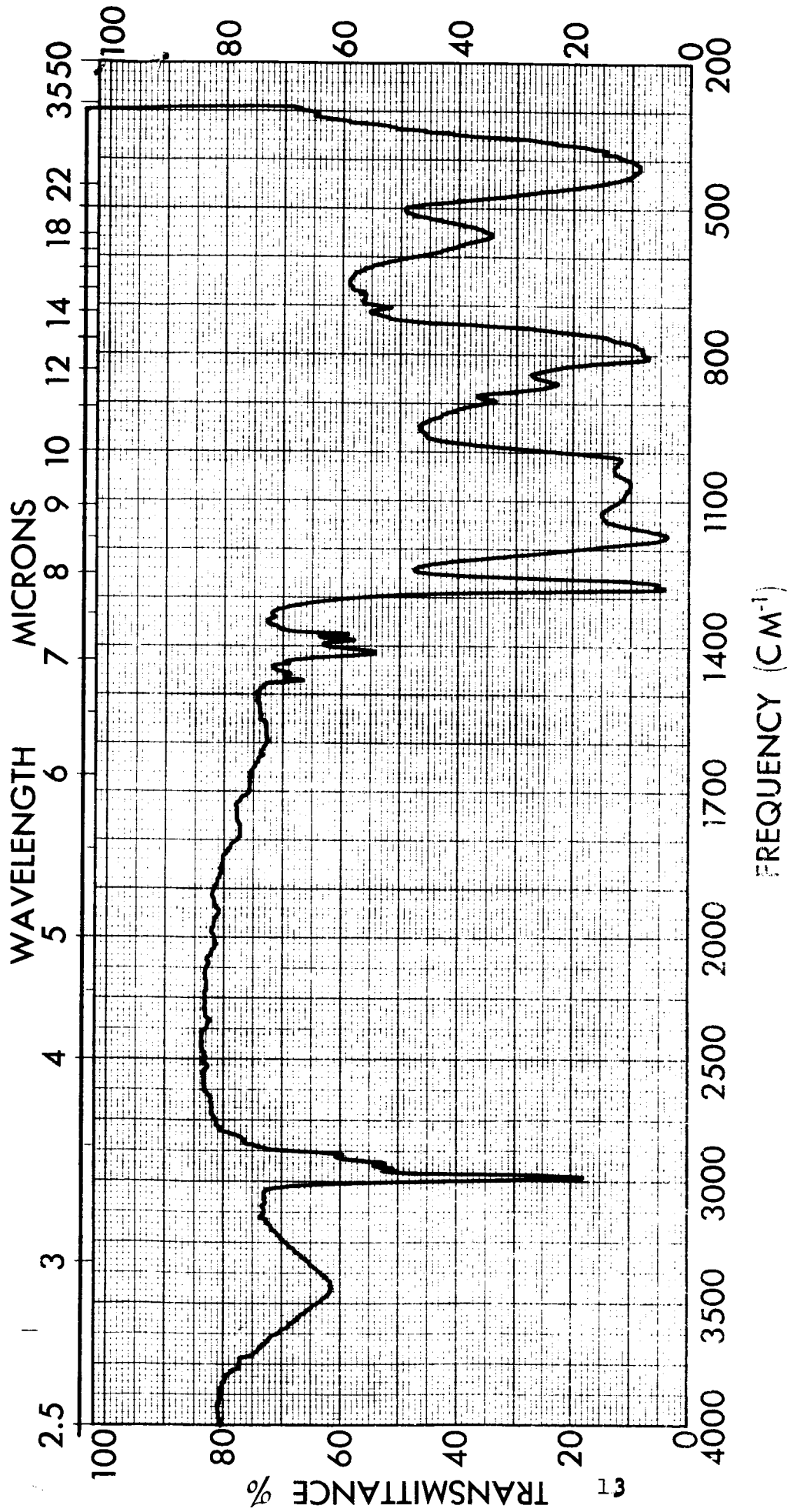Figure 3.   Specular Reflectance Spectrum of CdS Cell
            Overcoated with Aluminum

WAVELENGTH   MICRONS

TRANSMITTANCE %

FREQUENCY (CM⁻¹)

Spectrum No. G-1754

Sample: Aluminum (on alumina sheets silicone primer)

Origin: AN 65287

Phase: Solid

Date: 8-19-65

Remarks: Specular Reflectance Spectrum

Figure 4   Specular Reflectance Spectrum of Silicone Primer on Aluminum
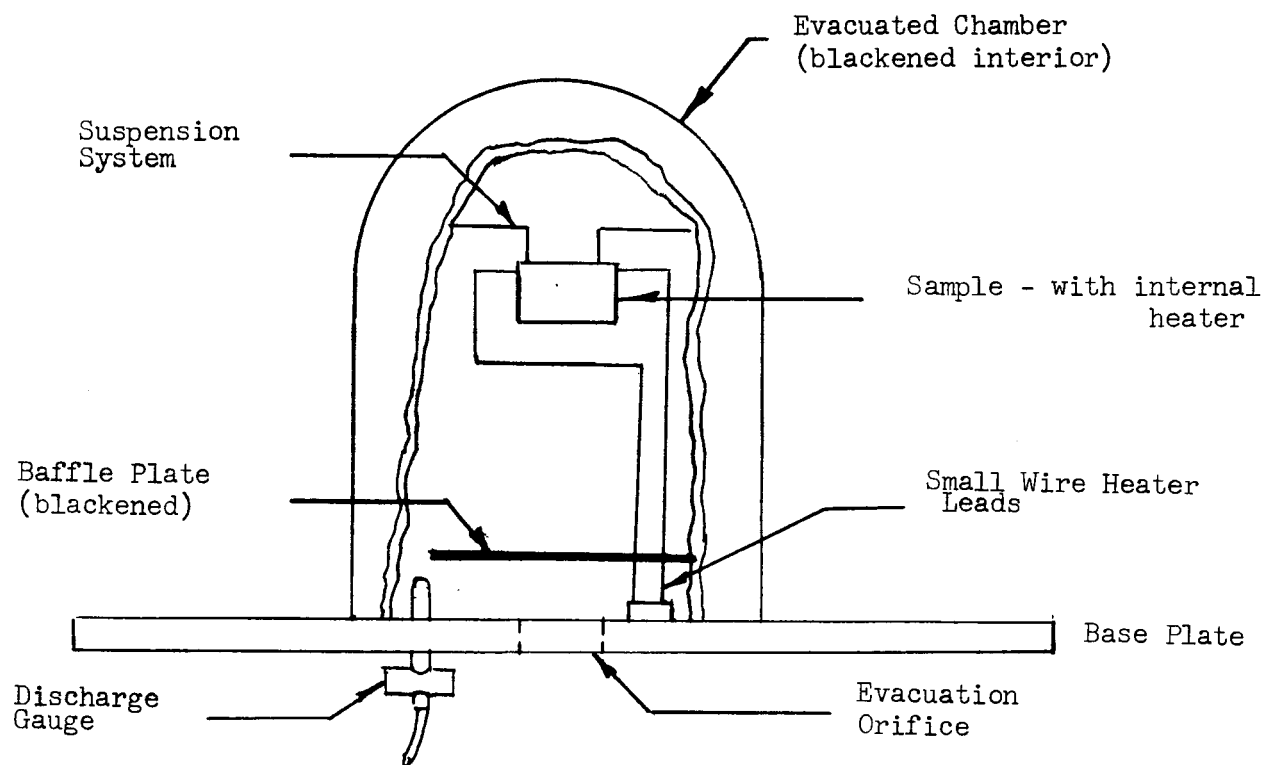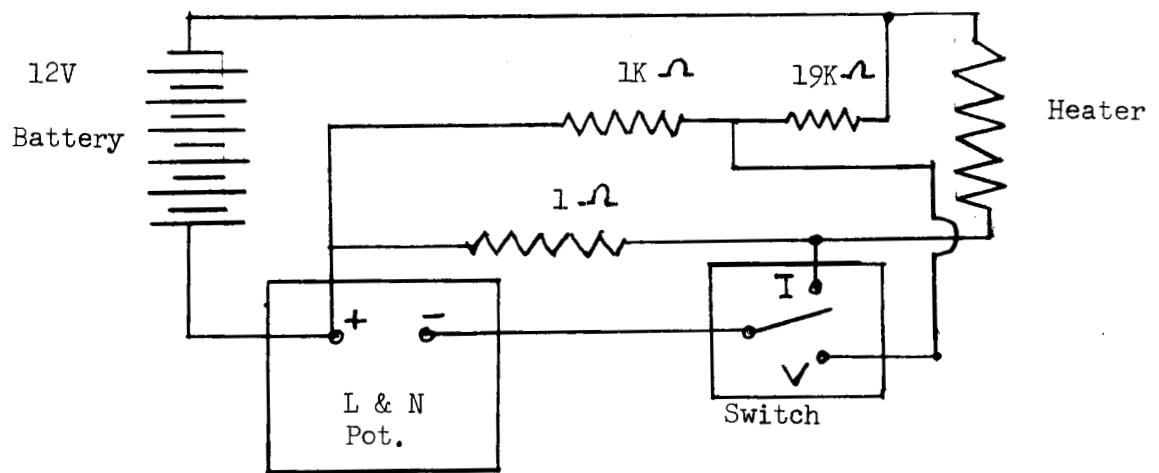
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Figure 5. Emittance Measurement Apparatus

Figure 6. Measuring Circuit - Power & Temperature