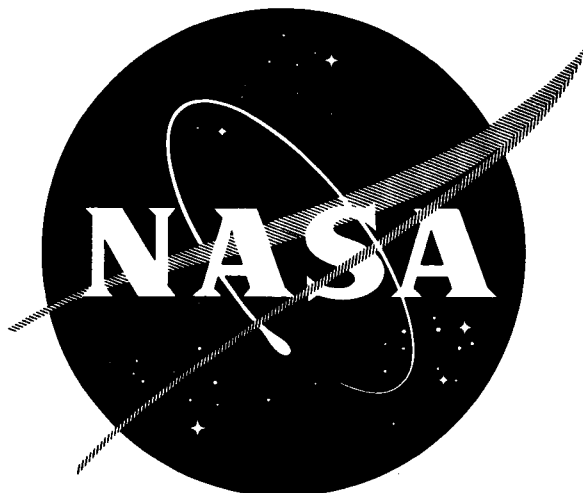NASA-CR-
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*Call
Betty
Carter*

EMISSIVITY COATINGS
FOR LOW-TEMPERATURE
SPACE RADIATORS

Quarterly Progress Report No. 2
For Quarter Ending 31 December 1965
CONTRACT NAS-3-7630

Prepared for
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
LEWIS RESEARCH CENTER
CLEVELAND, OHIO

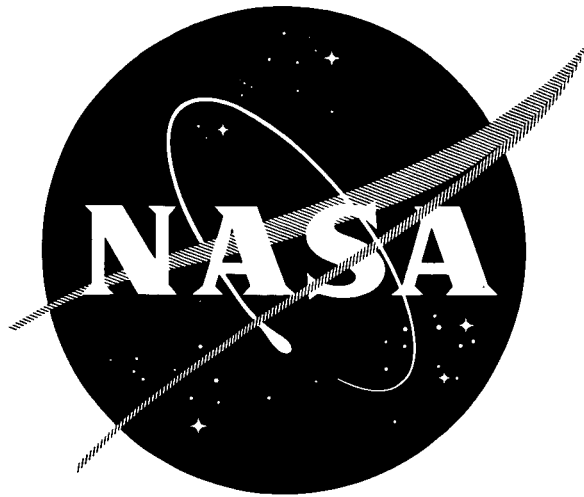GPO PRICE $ _____

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Aerospace Sciences Laboratory
Lockheed Palo Alto Research Laboratory
LOCKHEED MISSILES & SPACE COMPANY
Sunnyvale, California

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Prepared by: Approved by:
F. J. Smith and J. G. Grammer   G. R. Cunnington
Sr. Thermodynamics Engineers   Project Leader

Aerospace Sciences Laboratory
Lockheed Palo Alto Research Laboratory
LOCKHEED MISSILES & SPACE COMPANY
Sunnyvale, California

FOREWORD

The results of the research activities carried out during the second quarterly period (1 October through 31 December 1965) of Contract NAS 3-7630, entitled Emissivity Coatings for Low-Temperature Space Radiators, are reported in this document. This work is being done by Lockheed Missiles & Space Company for the Lewis Research Center of the National Aeronautics and Space Administration.

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ILLUSTRATIONS

TABLE

Section 1
INTRODUCTION AND SUMMARY

The major objective of this program is the evaluation of candidate coatings for low-temperature spacecraft radiators having long operational lifetimes. The surfaces must show a high total hemispherical emittance at operating temperature with a low absorptance to energy in the solar spectrum; the latter is important because of the low operating temperature level of some radiators, 530°K or less. The stability of the radiative properties of the coating in the space environment is a critical factor as changes in either absorptance or emittance during the mission would result in severe problems with the operating power system. Since little is presently known about the long-term behavior of coatings considered for use on these low-temperature radiators, a program was established to evaluate both organic and inorganic coatings. The object of the initial program was the evaluation of the properties and stability of candidate coatings under conditions of exposure to ultraviolet radiation, vacuum, elevated temperatures, and temperature cycling. During the first phase of the program, candidate materials will be exposed simultaneously to ultraviolet radiation at a 1-sun level, maximum operating temperature, and vacuum of 10^{-7} Torr or less for 500-hr periods. The second phase of the program will be the exposure of two materials selected on the basis of the results of the initial phase for 5,000 hr.

The tasks undertaken during the second quarterly period and the accomplishment under each were as follows:

- The literature survey to provide up-to-date information on the coatings as well as provide data for the selection of a sixth coating was continued.
- The exposure apparatus was checked, and initial calibration data were obtained.
- All test specimens of three of the five coating systems were received, and pretest optical property measurements were made.

Detailed discussions of the activities for this quarter are presented in the following sections.

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Section 2
LITERATURE SURVEY

During the period covered by this report several major findings have been reported which bear directly upon the objectives of this program. Under a NASA-Marshall Space Flight Center contract (NAS-8-11266) LMSC has investigated solar radiation-induced damage to the optical properties of zinc oxide (Ref. 1). That program succeeded in demonstrating that the damage mechanism for ZnO pigments was based on a photochemical evaluation of oxygen. Furthermore, on the basis of the first reported in situ measurements of u-v radiation damage in vacuum, it was conclusively demonstrated that u-v degraded zinc oxide rapidly recovered its initial optical properties upon re-exposure to air.

Further in situ measurements on zinc oxide and titanium dioxide pigmented silicone paints, along with a detailed description of the LMSC in situ bidirectional reflectance apparatus was reported (Ref. 2) at the AIAA Thermophysics Specialists Conference, Monterey, Calif; September 1965. That report specifically indicated that white pigmented silicone thermal control paints exhibit the same damage and recovery phenomena as the free pigments.

At the same meeting, preliminary results from the Ames emissivity experiment on OSO-II were reported (Ref. 3). These results are of immediate interest since four of the coatings flown were identical to those being examined under this program (titanium dioxide/silicone), zinc oxide/silicone, zinc oxide/potassium silicate, and zirconium silicate/potassium silicate). The results for the zinc oxide and titanium dioxide pigmented silicones were in substantial agreement with the laboratory in situ results. However, gross disagreement was observed between the flight data and conventional pre- and post-test measurements. On the other hand, the inorganic coatings appeared to be more stable than pre- and post-test laboratory measurements indicated.

The results of the in situ measurements coupled with the flight data lead to the incontestable conclusion that all prior u-v radiation test data based on pre- and post-test measurements of optical properties performed in air must be critically re-examined. For this reason, considerable data of this nature which have been published during the period of this report have not been included.

Section 3
EXPERIMENTAL APPARATUS

3.1 DESCRIPTION OF APPARATUS

The complete experimental apparatus which was described in detail in Ref. 4 remains unchanged except for the modification of the xenon source optics. The u-v source is a 900-W Hanovia xenon lamp, Model 538-CL, that is mounted in an Orion Optics Corp., universal lamp housing, Model C-60-50-5-15. This lamp housing used a 2-in. focal length, 1.5 in. diameter quartz condensing lens as a collector. The energy collected by the lens is augmented by the use of a spherical mirror placed behind the lamp to re-image the arc back on itself. In the process of relative spectral calibration of the xenon source, a difficulty arose when the bright spot near the cathode was used as a source to obtain a uniform approximately collimated beam. It became evident that the percentage of energy in the u-v region increased as the image distance increased. With the lens set so that a nearly uniform intensity was produced over an area 2-in. in diameter at a distance of 15 in. from the lamp housing (approximately the distance to the sample) the percentage of energy in the u-v band was 25% of the total energy, not the desired 11.8%. This change was related to the difference in focal length of the quartz lens for the ultraviolet and near infrared. The effect of this chromatic aberration may be reduced by using a longer focal length lens. The original equipment lens has been replaced with a quartz 4.5-in. focal length lens of the same diameter. Satisfactory results have been obtained with the updated optical system.

3.2 RESULTS OF INITIAL OPERATIONS

The initial operation of the exposure apparatus commenced with a bake-out of the chambers at approximately 250°F using sorption pumps to remove the initial gas load. After bake-out, pumping with the electronic pumps was satisfactory.

A pressure of 10^{-7} Torr was obtained without the liquid nitrogen cold wall being filled. After approximately one week of operation, erratic pump performance was observed. The problem was traced to a badly contaminated high voltage feedthrough in the electronic pump which resulted in a high leakage current that inhibited proper pumping. The contaminated parts were cleaned and the pumps restarted. Satisfactory operation was achieved for a short time, but subsequent inspection of the feedthrough indicated the contamination was again present. The pump manufacturer stated this contamination was the result of a faulty plating process during manufacturing. The manufacturer provided new parts for the pump at no cost.

Calibration of the u-v source was completed utilizing the modified optical system. The irradiance of the lamp unit was measured in air at a distance of 15.5 in. from the front of the lens holder of the lamp unit. The irradiance was measured as a function of input power. The detector was a calibrated Epply thermopile and its output was measured by a Kiethley voltmeter.

Figure 3-1 shows the measured irradiance of the lamp unit at a distance of 15.5 in. (the distance of the sample in the chambers from the front of the lens holder) in air. These values include the transmission of the chamber special window. The irradiance of the lamp unit in the u-v transmission band of the Corning 7-54 filter was also measured in air. A calibrated Epply thermopile was used as a detector. The u-v irradiance in the transmission band was measured by measuring the transmission of the 7-54 for the source energy and then measuring the transmission of a combination 7-54 and 3-72 filter for the source. The spectral transmission of these filters are shown in Fig. 3-2. The energy in the 0.22 to 0.43 band is calculated after correcting for the transmission of the 7-54 band and the 3-72 filter. The irradiance of the lamp unit at the sample distance in the wavelength band 0.22 to 0.43 μ is shown in Fig. 3-3. A 617-W input is required for the lamp for its operating level to provide the u-v energy output to match the solar radiance in the 0.2 to 0.4 μ wavelength region. The irradiance of the beam as a function of distance from the lamp unit around the sample position is shown in Fig. 3-4. A traverse across the beam at the sample position is shown in Fig. 3-5.

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The relative spectral irradiance of the lamp unit, Fig. 3-6, was measured with a calibrated radiometer consisting of a monochromator and a photomultiplier detector. A MgO reflectance plate was used to provide uniform illumination of the entrance slit of the monochromator. The monochromator and detector unit was calibrated by comparison with the irradiance of a tungsten standard lamp which was calibrated by NBS.
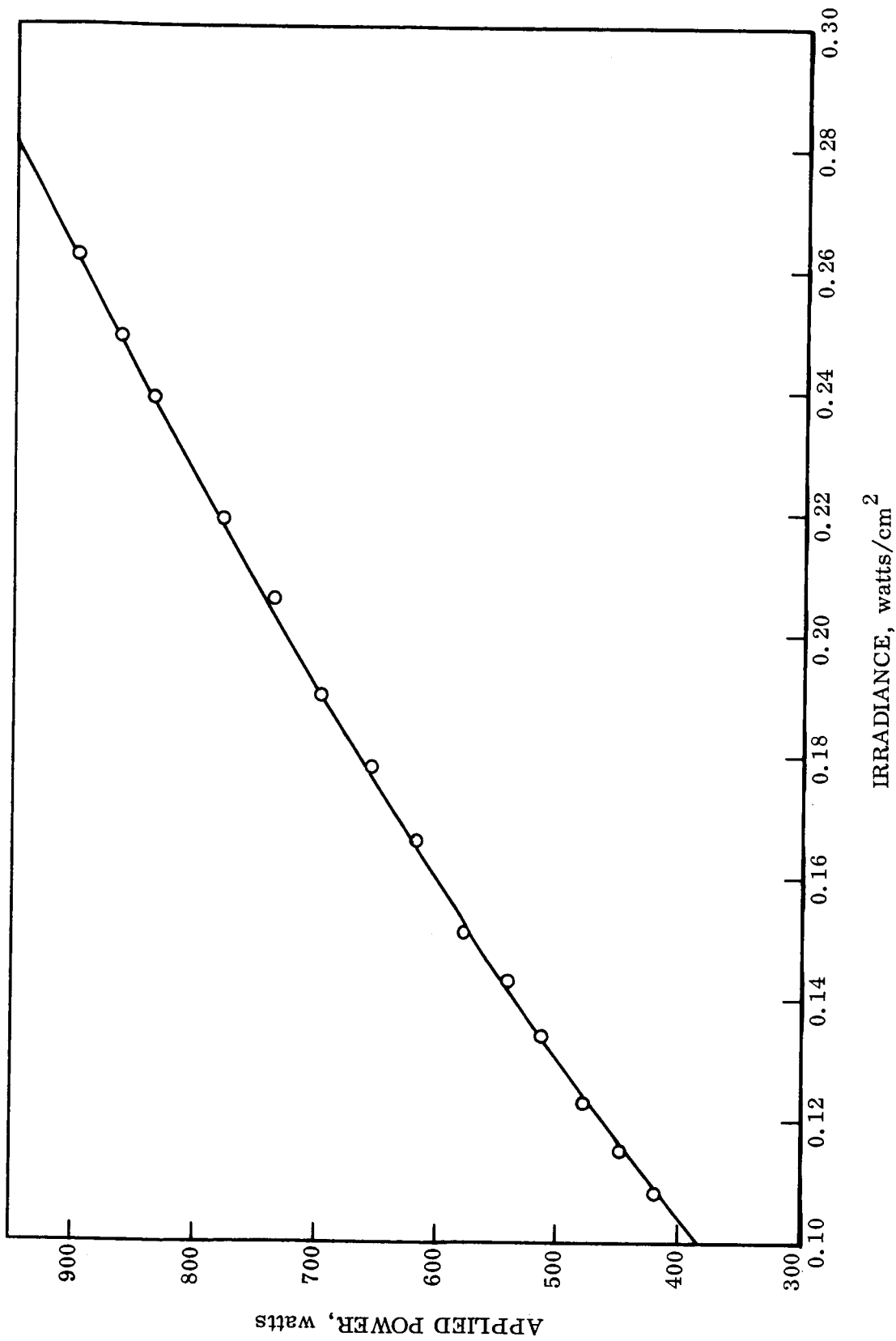
Fig. 3-1 Total Irradiance of Lamp Unit

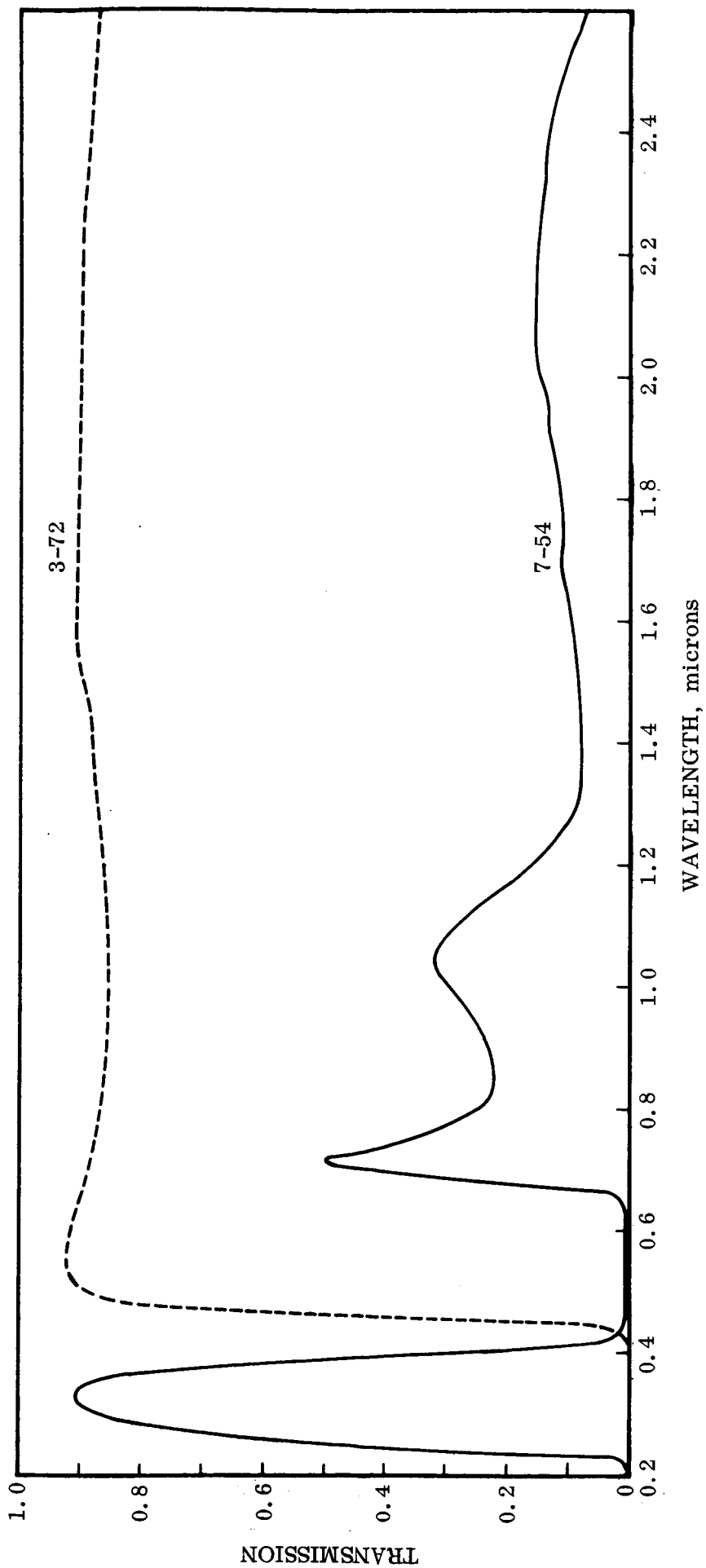APPLIED POWER, watts

IRRADIANCE, watts/cm^2
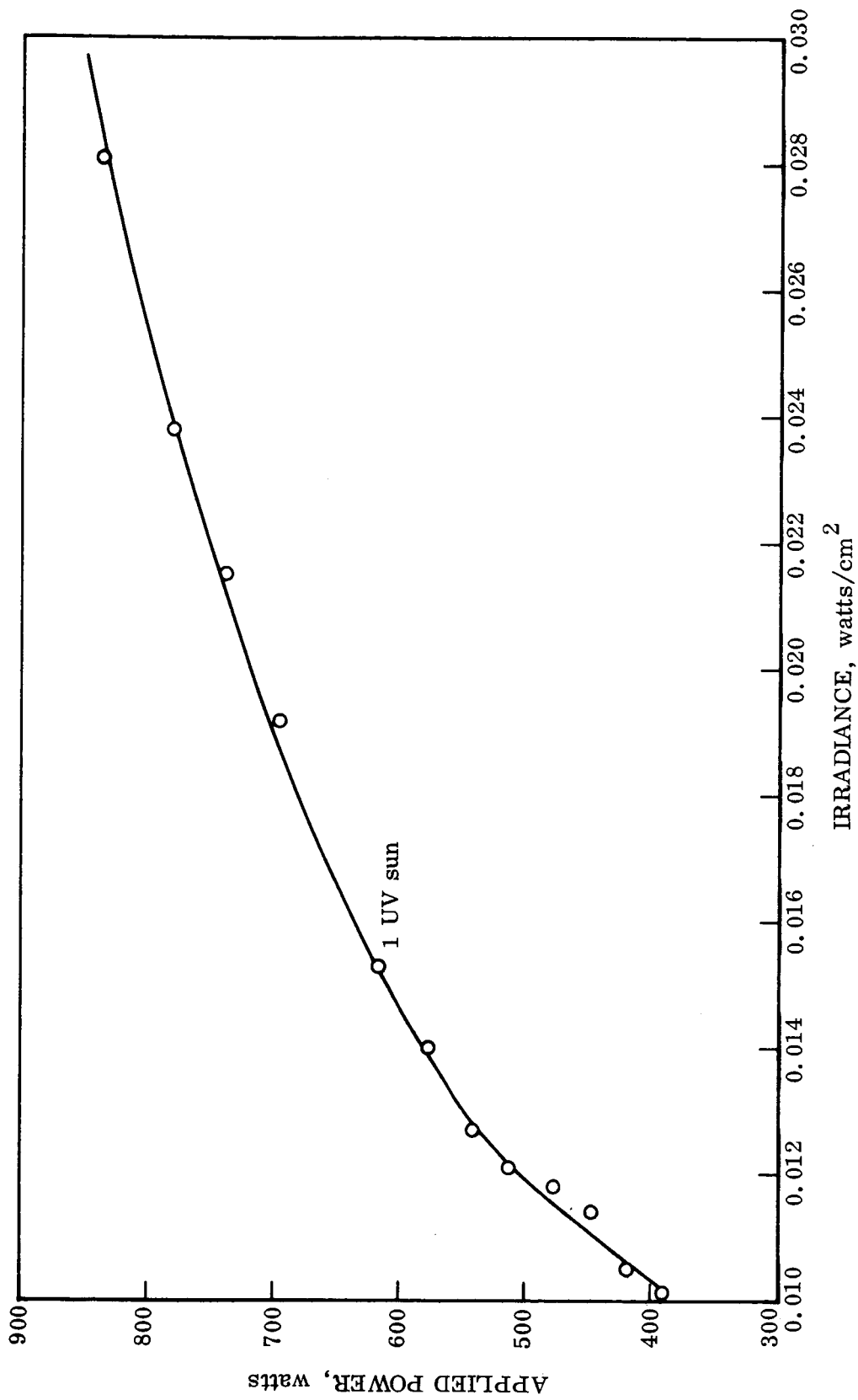
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Fig. 3-2 Filter Transmissions

8

Fig. 3-3 Irradiance for Band Energy From 0.22 to 0.43 μ of Lamp Unit
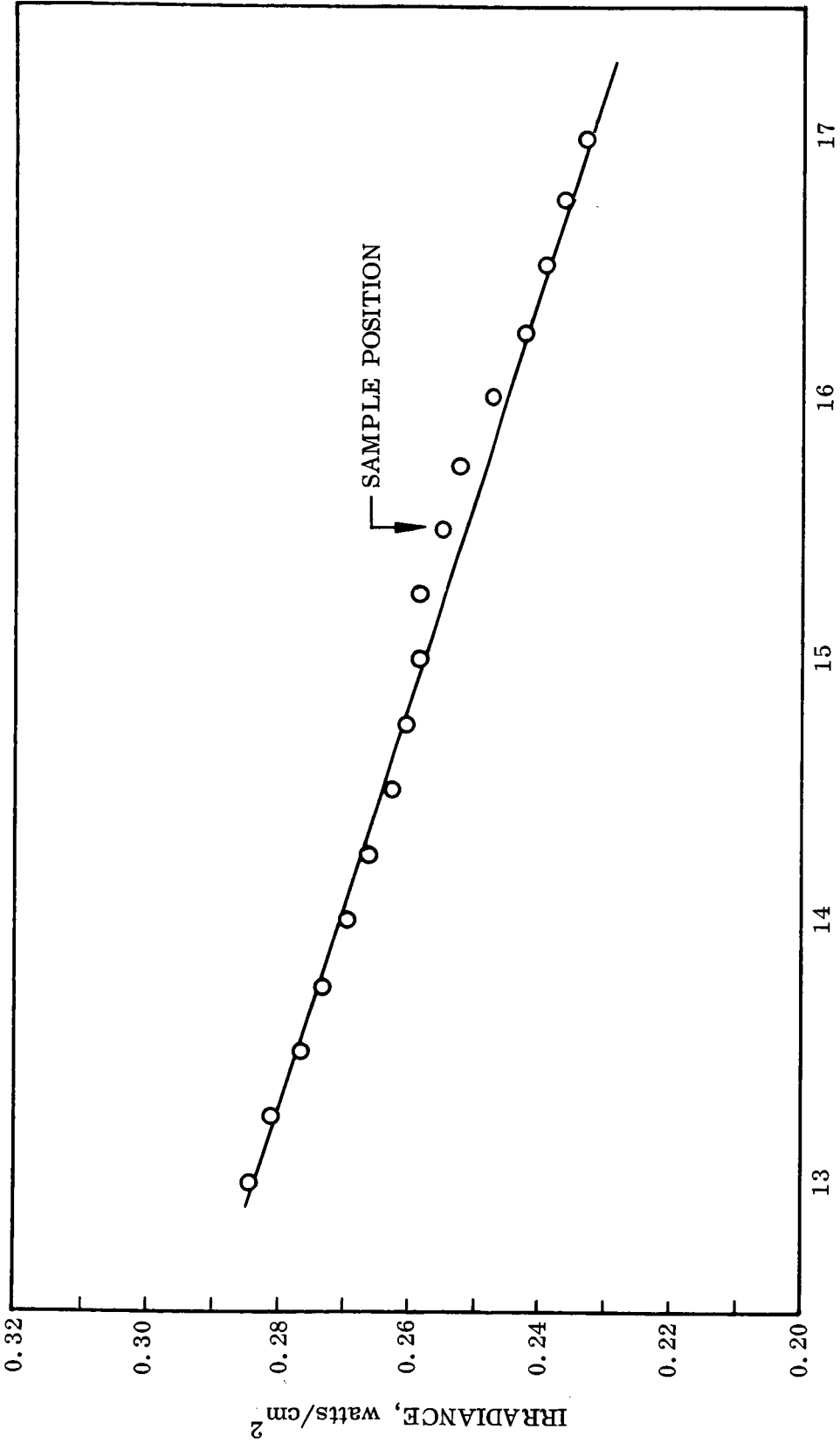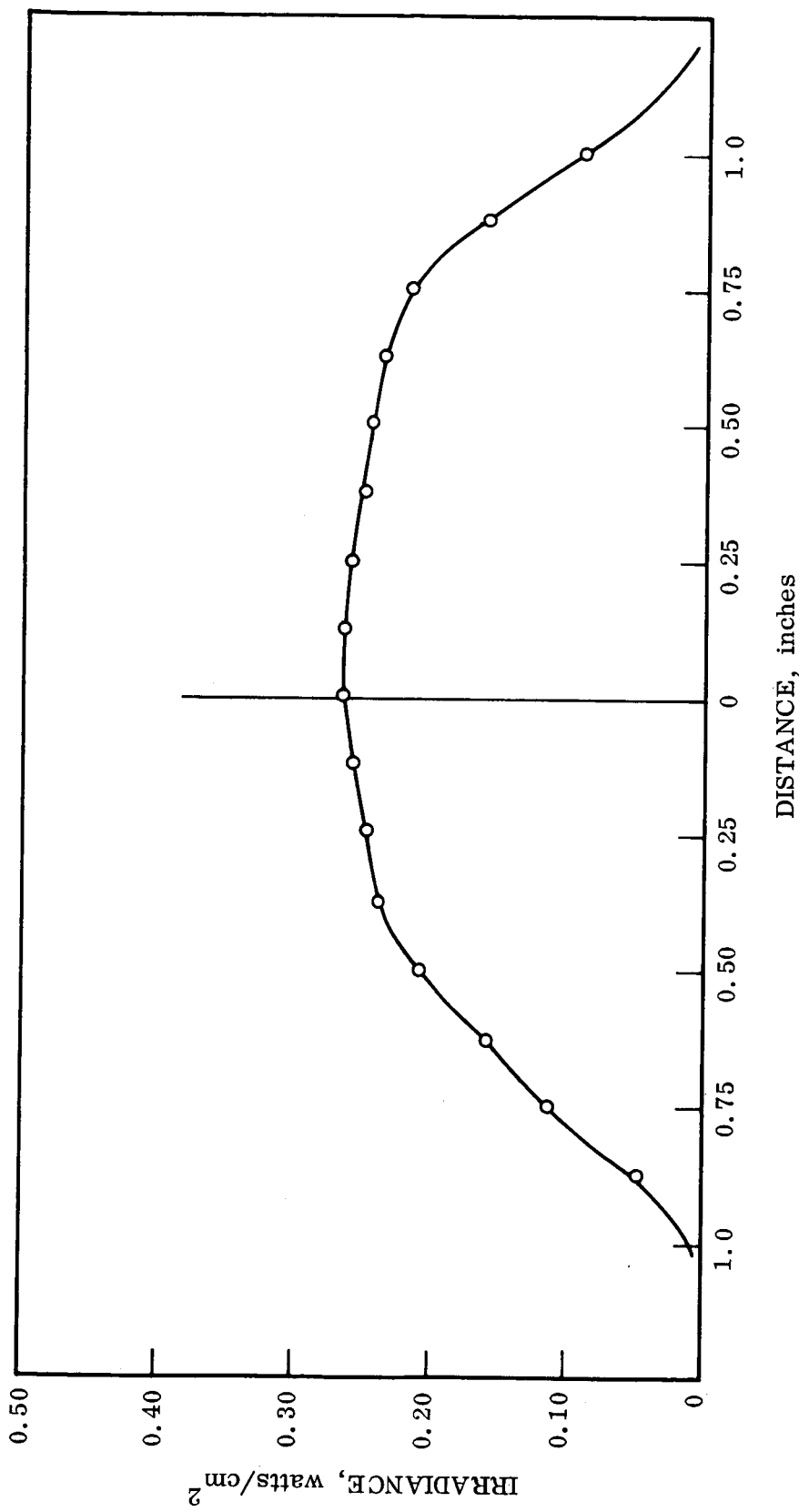
Fig. 3-4 Irradiance as a Function of Source Distance

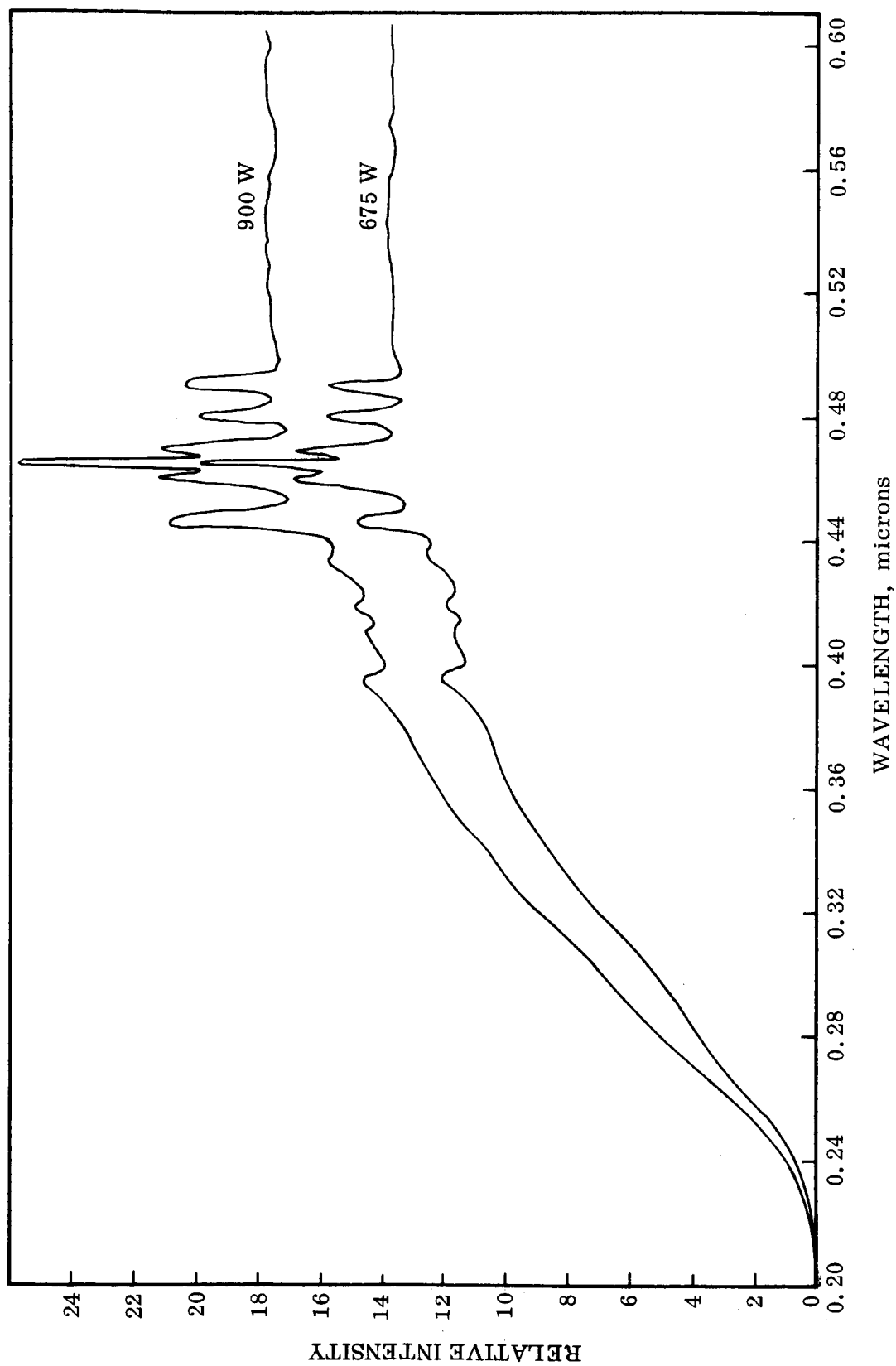Fig. 3-5 Transverse Energy Distribution of Lamp Beam

Fig. 3-6 Relative Spectral Distribution of Lamp Energy to 0.55 μ

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Section 4

PROPERTIES OF CANDIDATE COATING

4.1 DESCRIPTION OF COATINGS

Test specimens of three candidate coatings have been received during the report period. The specimens on hand are the Hughes Aircraft Co., $Al-SiO_4/K_2SiO_4$, the LMSC TiO_2/silicone, and the LMSC $ZrSiO_4/K_2SiO_4$ coatings. These coatings are described in detail below. The initial optical properties are also presented.

4.1.1 Thermatrol -A100 (TiO_2/silicone)

Source and Cost − Lockheed Missiles & Space Company; price variable depending on quantity; nominal price is $60 per gallon.

Starting Composition − Polymethyl-vinyl siloxane elastomer plus TiO_2 pigment, 1:1 by weight.

- Vehicle: Dow-Corning proprietary, Q92-009, 33% non-volatile content by weight, 24 hr at 70°C

Flash Point	60 to 65°F
Viscosity, cps	15,000
Specific Gravity	0.835
Diluted with VM and P Naptha	

- Pigment: Titanox RA-NC, Titanium Pigment Corp., proprietary; calcined rutile TiO_2, 93% TiO_2.

Particle Shape and Size − The weighted average particle size is $0.3\,\mu$. The particles are spherical.

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Substrate — 1-in. diameter disc, 0.050 in. thick of 6061 T-6 aluminum machined to a 30 rms finish.

Method of Application — The finish is applied by spray techniques conforming to MIL-F-18264 specifications. Prior to applying the top coat, the entire surface is primed with one coat of silicone primer, Dow Corning Corp. A-4094 or equivalent, to a thickness of approximately 0.2 mils. The primer is air cured 30 min minimum prior to application of top coats. Thickness and cure times for the top coat are as follows:

> Total dry film thickness, including primer, 3.5 to 5.0 mils
> Curing time; 24 hr minimum after final coat

Coating Thickness — 3.5 to 5.0 mils.

Density — 1.5 gm/cm^3

Weight Loss During Vacuum Testing — Negligible after coating has been fully cured.

Final Composition — Specific gravity after curing (7 days at 150°F and 50% RH); non-pigmented 1.15; pigmented 1.50.

4.1.2 LP 10A ($ZrSiO_4/K_2SiO_4$)

Source and Cost — Lockheed Missiles & Space Company; price variable depending on quantity; nominal price $740 per gallon.

Starting Composition —

- Pigment to binder ratio: 3.5 to 1 by weight
- Pigment: Metals and Thermit Corp, 1000W grade, "Ultrox" zirconium silicate, acid leached and calcined by LMSC
- Binder: potassium silicate

Particle Shape and Size — Particle shape, angular; particle size, < 1.0 μ.

Substrate — 1-in. diameter disc, 0.0050 in. thick of 6061 T-6 aluminum machined to a 30 rms finish.

Method of Application — Standard spray gun techniques, base coat reacts with substrate and serves as primer; room temperature cure, approximately 12 hr.

Coating Thickness — 3.0 to 5.0 mils.

Density — 4.0 gm/cm^3

Weight Loss During Vacuum Testing — Less than 5.0%.

Final Composition — Zirconium silicate-potassium silicate composite (exact chemical composition not known).

4.1.3 Hughes Inorganic White Coating (Al-SiO$_4$/K$_2$SiO$_4$)

Source and Cost — Hughes Aircraft Co.; cost figures not stated by supplier.

Starting Composition —

- Pigment to binder ratio: 4.4 to 1 by weight
- Pigment: A naturally occurring china clay primarily aluminum silicate; approximately 3.0% impurity level, namely Fe-0.70% Ti 0.42%, Ca 0.05%, Mg-1.28%, Na-0.47% and K-0.11%; the clay is calcined at 1275°C, then ball milled for 12 hr with water.
- Binder: Sylvania PS-7 electronic grade potassium silicate

Particle Shape and Size — Particle size following milling less than 200 mesh; particle shape is typical of a china clay.

Substrate − 1 in. diameter disc, 0.050 in. thick of 6061 T-6 aluminum machined to 30 rms finish.

Method of Application − The coating is applied in three coats, each coat being baked for 1 hr at 225°F and the final coating baked for 1 hr at 260°F. An air brush is used for painting.

Coating Thickness − 6.0 to 8.0 mils after curing.

Weight Loss During Vacuum Testing − The procedure is covered by Hughes Materials and Process Specification, HMS 15-1374 and HP 4-135. A typical weight loss is 0.02% when exposed to vacuum at 250°F; the weight loss is water vapor.

Final Composition − Not known.

4.2 INITIAL OPTICAL PROPERTIES

The initial optical properties, the solar absorptance (α_s) and the infrared emittance (ϵ), have been determined and are tabulated in Table 4-1. Typical spectrum reflectance curves for each of the coatings are presented in Figs. 4-1 through 4-3. Data obtained by use of the Cary spectrophotometer and the Gier-Dunkle intergrating sphere are presented for comparison. The emittance values reported were obtained by use of the Lion Research Corp. Optical Surface Comparator described in Ref. 4.

The solar absorptance of test samples was determined by two separate procedures. The first method was by measurement of the spectral reflectance on a Cary Model 14 spectrophotometer with an integrating sphere attachment. This instrument has been described previously (Ref. 4). The resulting spectral data are then integrated against the Johnson (Ref. 5) curve to obtain solar reflectance from which the solar absorptance is inferred from Kirchoff's law.

Table 4-1

INITIAL ROOM TEMPERATURE OPTICAL PROPERTIES

Sample	Source	Coating	Solar Absorptance		Emittance (Optical Surface Comparator)
			Gary	Gier-Dunkle	
1	LMSC	TiO_2/silicone	0.15 ± 0.02	0.17 ± 0.01	0.88 ± 0.03
2	LMSC	TiO_2/silicone	0.15 ± 0.02	0.16 ± 0.01	0.82 ± 0.03
3	LMSC	TiO_2/silicone	0.15 ± 0.02		0.91 ± 0.03
4	LMSC	TiO_2/silicone	0.18 ± 0.02[a]	0.19 ± 0.01	0.85 ± 0.03
5	LMSC	TiO_2/silicone	0.15 ± 0.02		0.85 ± 0.03
6	LMSC	TiO_2/silicone	0.15 ± 0.02		0.85 ± 0.03
7	LMSC	TiO_2/silicone	0.15 ± 0.02		0.87 ± 0.03
8	LMSC	TiO_2/silicone	0.15 ± 0.02		0.86 ± 0.03
9	LMSC	$ZrSiO_4$/K_2SiO_4	0.11 ± 0.02	0.11 ± 0.01	0.91 ± 0.03
10	LMSC	$ZrSiO_4$/K_2SiO_4	0.11 ± 0.02		0.87 ± 0.03
11	LMSC	$ZrSiO_4$/K_2SiO_4	0.14 ± 0.02	0.15 ± 0.01	0.90 ± 0.03
12	LMSC	$ZrSiO_4$/K_2SiO_4	0.11 ± 0.02		0.90 ± 0.03
13	LMSC	$ZrSiO_4$/K_2SiO_4	0.13 ± 0.02		0.91 ± 0.03
14	LMSC	$ZrSiO_4$/K_2SiO_4	0.11 ± 0.02	0.11 ± 0.01	0.90 ± 0.03
15	LMSC	$ZrSiO_4$/K_2SiO_4	0.14 ± 0.02		0.90 ± 0.03
16	LMSC	$ZrSiO_4$/K_2SiO_4	0.10 ± 0.02		0.90 ± 0.03
19	Hughes	$AL-SiO_4$/K_2SiO_4	0.14 ± 0.02	0.14 ± 0.01	0.90 ± 0.03
20	Hughes	$AL-SiO_4$/K_2SiO_4	0.14 ± 0.02	0.14 ± 0.01	0.88 ± 0.03
21	Hughes	$AL-SiO_4$/K_2SiO_4	0.14 ± 0.02		0.90 ± 0.03
22	Hughes	$AL-SiO_4$/K_2SiO_4	0.14 ± 0.02		0.90 ± 0.03
23	Hughes	$AL-SiO_4$/K_2SiO_4	0.14 ± 0.02		0.89 ± 0.03
24	Hughes	$AL-SiO_4$/K_2SiO_4	0.14 ± 0.02		0.88 ± 0.03
25	Hughes	$AL-SiO_4$/K_2SiO_4	0.14 ± 0.02		0.90 ± 0.03
26	Hughes	$AL-SiO_4$/K_2SiO_4	0.13 ± 0.02		0.90 ± 0.03

(a) Coating not of proper thickness (< 5 mil).

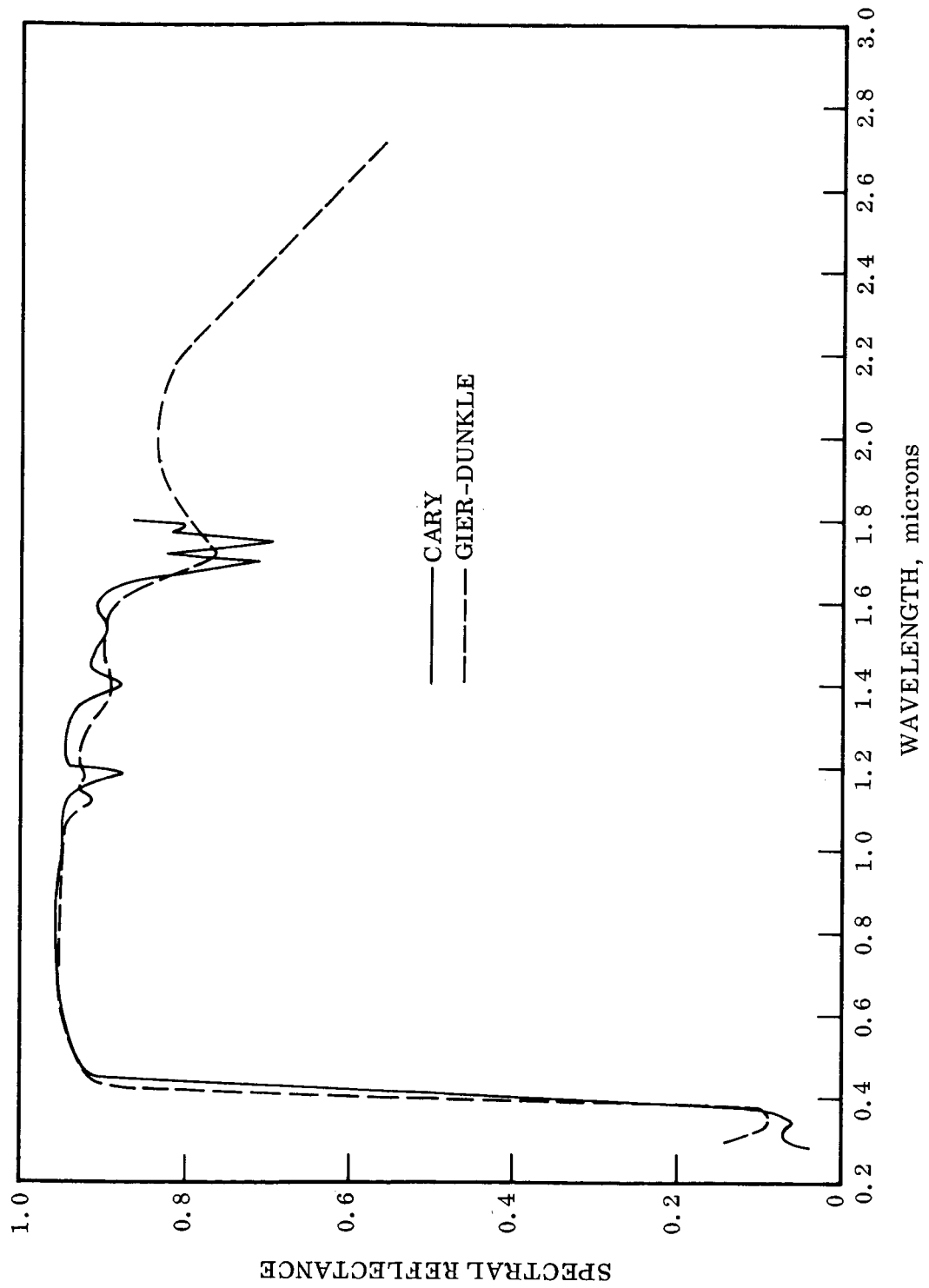Fig. 4-1 Typical Spectral Reflectance of TiO$_2$/Silicone Coating
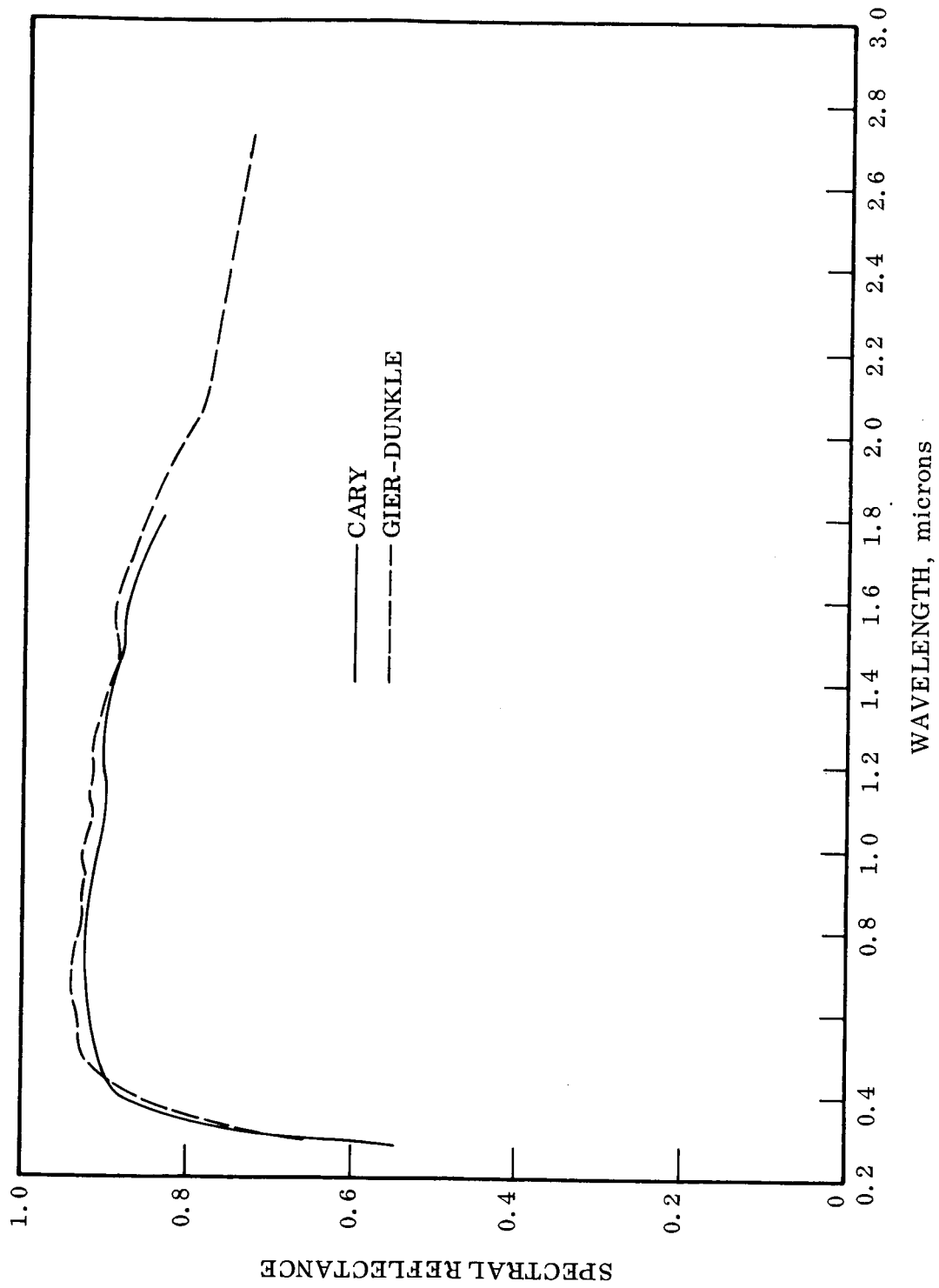
Fig. 4-2 Typical Spectral Reflectance of $ZrSiO_4/K_2SiO_4$ Coating

WAVELENGTH, microns

SPECTRAL REFLECTANCE

CARY
GIER–DUNKLE
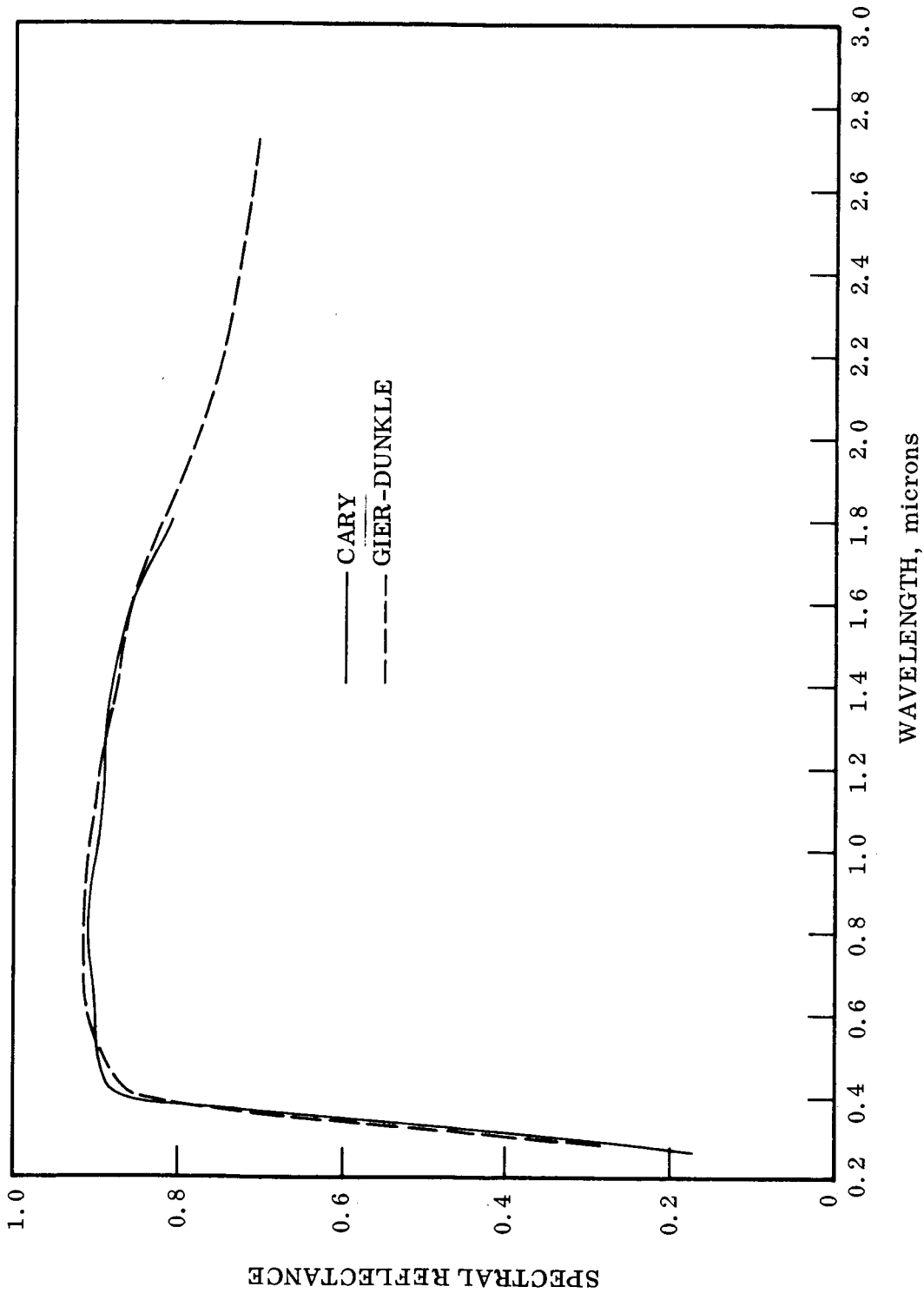
Fig. 4-3 Typical Spectral Reflectance of $AlSiO_4/K_2SiO_4$

The Cary sphere is small and has relatively large apertures for entrance and exit of sample, reference, and sphere illumination beams. The sphere is illuminated by external optics and the reflected sample energy is directed to the entrance slits of the monochromator. Because of large apertures, a bright spot from the illuminating beam, and the small sphere size, it is obvious that the instrument has significant sources of error. The absolute magnitude of error is considerably reduced by establishing operational procedures which circumvent the major difficulties. Normal operations in this laboratory calls for calibration of the system against a known first surface aluminum mirror. This is done by setting reflectance values at each wavelength to correspond to the known mirror properties. Unknown samples are then run, and the reading is obtained in absolute reflectance units. This procedure minimizes but does not eliminate effects of the apertures and bright spot. The data obtained are relative in the sense that the instrument is initially calibrated against a known surface. Therefore, continuous checks must be made to assure the validity of the values used for the calibration. The instrument is used as a control for large numbers of samples since it is easily operated, is fast, and within limits has reasonable accuracy. Where changes in spectrum or comparisons among identical samples are desired it is a highly useful laboratory tool.

In view of the relative nature of Cary results it is also necessary to obtain a limited number of absolute measurements to verify the Cary spectrum. These measurements are performed on a single beam Gier-Dunkle integrating sphere attached to a Perkin-Elmer, Model 98 monochromator. This sphere is much larger than the Cary (9.5 in. diameter), has only two small apertures (entrance port 1 in. diameter, detector area ~ 1-in. diameter), and does not suffer from direct sample illumination of the detector. The sample is centrally mounted in the sphere and may be rotated at angles from 0 to 90 deg relative to the entrance port. When the sample is normal to the port its shape factor to the hole is approximately 0.011. This construction permits direct measurements of the absolute reflectance of test samples and also permits cross checks which verify the validity of data obtained.

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In normal operation a 1-in. disc sample is mounted on the sample holder and rotated 10 deg off axis from the entry port. Monochromatic energy is then directed alternatively to the sphere wall and then to the sample. Detector response is rated for each beam position with the ratio of response being directly the absolute reflectance of the sample. This procedure is repeated for each required wavelength throughout the spectral region 0.275 to 2.75 μ. The data are then integrated against the Johnson curve to obtain the solar absorptance.

The Gier-Dunkle instrument has an inherent accuracy of 1% in determination of spectral reflectance and can be cross checked to assure that operation is producing this precision. Sample rotation may also be used to determine the extent of entry port losses so corrections can be applied for this effect. However, because of its manual operation the measurements are time consuming and must be accomplished by highly skilled personnel. Therefore, only a limited number of such determinations are made on test samples.

When initial measurements are made using the Gier-Dunkle sphere and the results used to calibrate Cary measurements on identical samples, it is possible to obtain accuracies of ± 2% in reflectance. This procedure is often used where large numbers of identical surfaces must be measured.

Section 5
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5. F. S. Johnson, ed., Satellite Environment Handbook, Stanford University Press, 1961