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Quarterly Progress Report

2nd Contract Period
August 16, 1977 to November 16, 1977

for the contract entitled

Development of Surfaces Optically Suitable for Flat Solar Panels
Contract No. NAS8-32481

(NASA-CR-150539) DEVELOPMENT OF SURFACES
OPTICALLY SUITABLE FOR FLAT SOLAR PANELS
Quarterly Progress Report, 16 Aug. - 16 Nov.
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A. Work Performed During Reporting Period and Future Work

Introduction:

This report is a sequel to our first quarterly report under contract No. NAS8-32481. The goals of the project are aimed toward development of selective surfaces suitable for use in flat plate collectors. The first six months of the contract have been devoted to:

1. Literature surveys to determine properties and preparation methods of selective surfaces and their application to flat plate solar collectors. Of particular interest are theories which explain selectivity and criteria for optimization of surface properties under given application conditions.
2. Development of our own facilities for parameterization of selective surfaces. Among other things we have built a reflectometer suitable for measuring the surface properties of samples. The design is unique in that relative contributions of specular and diffuse components of the reflected beam are separately evaluated. At each data point reference is made to standard samples and we believe that the method of data analysis represents a new contribution to the techniques of reflectometry whereby reasonably accurate reflectance measurements can be made with simple instrumentation.
3. Development of an inexpensive selective coating for solar collector use. The surface described in our first quarterly report has been developed to the extent that it now rivals commercial surfaces in selectivity, absorptivity, and durability with significantly

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simpler fabrication procedures. We have also begun work on selective coatings for windows, both by literature surveys and laboratory experiments.

This report describes our innovations in reflectometry techniques, our development of an absorbing selective coating is discussed along with details of surface properties, and finally, we discuss conclusions as to the parameterization desired for practical applications of selective surfaces.

Reflectometry of Diffusely Reflecting Surfaces:

In general, evaluations of selective surfaces found in the literature have been accomplished through specular reflectance measurements. This is, of course, entirely valid under those circumstances where the surface is essentially specular. Many of the coatings used for solar absorbers are indeed primarily specular. Nevertheless, large errors can be made in reflectivity determinations for which the sample exhibits considerable diffuse reflectivity. This point was brought sharply to our attention by a factor of eight mismatch between two sets of data, made outside our laboratory, one done by a total reflectivity technique and the other by a specular technique.

Total reflectance measurements can be accomplished most accurately through a diffuse integrating sphere whereby the collection efficiency for reflected light is independent of angle. This method, however, suffers from sensitivity problems and is difficult to extend into the infrared. Other integrating approaches suffer from varying sensitivities for light reflected from different angles. Unless elaborate precautions are maintained the diffusely reflected light will usually be underemphasized so that the measured reflectivity of, for example, a gold sample may be several times that of an MgO coated sample even though the total hemispherical reflectivities are very nearly the same (~ 0.98 in the near infrared).

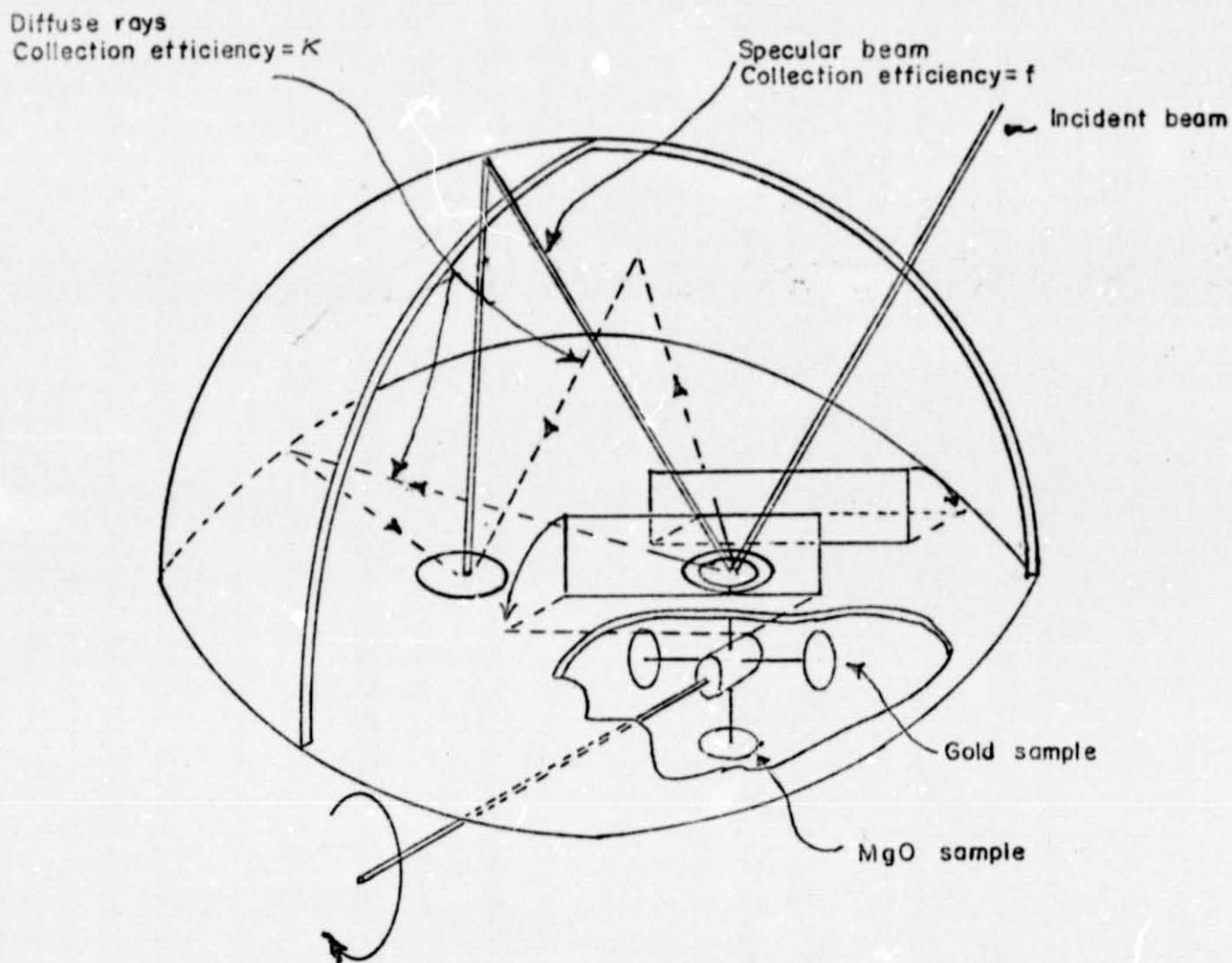
We have developed a procedure by which a simply constructed, inexpensive reflectometer can be used to assess both spectral and diffuse reflectivities. The basic reflectometer was described in our first quarterly report and consists of a gold plated hemisphere with detector and sample mount located along a basal diameter at equal distances from the center of the hemisphere

base (c.f. Fig. 1). The sample mount holds four samples which are alternately exposed to the incident beam of chopped dispersed light with accurate positional indexing. Two of the sample positions are usually occupied by evaporated gold on pyrex and freshly prepared magnesium oxide on aluminum. Both of these reflectivities are known to be close to unity for the spectral range of interest and are easily reproducible from sample to sample. A pair of "flaps" situated within the hemisphere can be positioned so that they either do not intercept any reflected light or intercept a fraction of the diffusely reflected light. The flap positioning is non-critical and need only remain constant during a single set of measurements at one wavelength as long as no portion of the specularly reflected beam is intercepted.

It is possible to divide the light reflected by a sample into two components: 1) a specular component, defined as the light included in the solid angle occupied by radiation which has been reflected from a specular surface, and 2) a diffuse component, which is the light occupying the remaining 2π radians in the hemispherical distribution. For perfect collection efficiency, the light power, R , detected by the reflectometer for sample irradiation I_o is

$$R = \rho_s I_o + \rho_d I_o \quad (1)$$

where ρ_s and ρ_d are the spectral and diffuse reflectivities defined as the fractions of light scattered into the specular and diffuse domains, respectively. For a nonideal system the measured value of R will be modified by the instrumental collection efficiency. In general this collection efficiency will differ for the two components with a smaller value for the diffuse



SCHEMATIC OF REFLECTOMETER OPTICS

Figure 1

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light and will depend on reflectance angle and detector and collector geometries. If f is the efficiency of collection for a purely specular sample, and assuming a reflectivity of unity for a specular gold surface, the gold intensity will be

$$R_{\text{Au}} = f I_o. \quad (2)$$

For a high reflectivity sample with a Lambertian distribution (i.e. $\propto \cos \theta$) of reflected light, such as MgO, let the collection efficiency be κ . Then the MgO intensity will be

$$R_{\text{MgO}} = \kappa I_o. \quad (3)$$

For an arbitrary sample the collected light intensity will be approximately given by R_s where

$$R_s = f \rho_s I_o + \kappa \rho_d I_o. \quad (4)$$

This expression contains a small error in accounting for the spatial overlap of the specular and diffuse distributions and assumes a Lambertian form for the diffuse component. This latter assumption will be correct for effectively incoherent surfaces (e.g., a fine powder) but will depart significantly for other cases as, for example, a regularly faceted surface with facet size greater than the irradiating wavelength.

From eqn. 4 it can be seen that the two reflectivities are

$$\rho_s = \frac{1}{I_o} \frac{\partial R_s}{\partial f}; \quad \rho_d = \frac{1}{I_o} \frac{\partial R_s}{\partial \kappa}. \quad (5)$$

While many schemes come to mind for the measurement of the derivatives in

eqn. 5 we have chosen to rearrange eqn. 4 by dividing through by eqn. 2;

$$\frac{R_s}{R_{Au}} = \rho_s + \frac{\kappa}{f} \rho_d \quad (6)$$

where $\frac{\kappa}{f}$ may be experimentally determined by the ratio of equation 3 to 2.

A similar equation may be obtained by inserting the flaps in Fig. 1 to block some of the diffuse component. The new intensity in this case is

$$\frac{R'_s}{R'_{Au}} = \rho'_s + \frac{\kappa'}{f} \rho_d \quad (7)$$

with κ'/f determinable by eqn. 3) with the flaps in position, i.e.

$$R'_{MgO} = \kappa' I_0 \quad (8)$$

A reflectivity determination can then be made for a given wavelength by measurement of R_{Au} , R_{MgO} , R'_{MgO} , R_s , and R'_s and simultaneous solution of eqns. 2, 3, 6, 7 and 8. This can be done by computer although hand reduction is fairly rapid because a closed expression for the 5 equations to be solved can be readily obtained. The accuracy of the method depends primarily on the accuracy to which R_s and R'_s can be determined; i.e., it can be shown that the error in ρ_s and ρ_d is

$$\frac{\Delta \rho_s}{\rho_s} = \frac{\Delta \rho_d}{\rho_d} = \frac{\Delta(R_s - R'_s)}{R_s - R'_s} \quad (9)$$

where $\Delta(R_s - R'_s)$ is the uncertainty in the measurement of these two quantities. If the collection efficiency is not reasonably good it is possible that $\Delta(R_s - R'_s)$ may be limited by instrumental sensitivity. We have encountered this problem in our instrumentation at the wavelength extremes of light sources due to the fact that our detector area is small (1 mm^2)

and hence a small value of κ/f is obtained because of the width of the diffuse image at the detector. A "perfect" focusing system (e.g., an ellipsoidal collector mirror) or a larger detector should eliminate this problem. Results for the diffuse reflectivity of a non-Lambertian surface will be lower than for Lambertian-like samples.

More rapid approaches to data gathering than the above procedure could involve chopping of the diffusely reflected light with direct readout of the two reflectivities through a small digital or analog computer. We would also like to note that the above analysis is justifiable on a more rigorous basis, but the essential elements of the procedure are contained above.

A reflectance curve obtained with this apparatus for a primarily diffuse surface is shown in Fig. 2 and compared with integrating sphere measurements.

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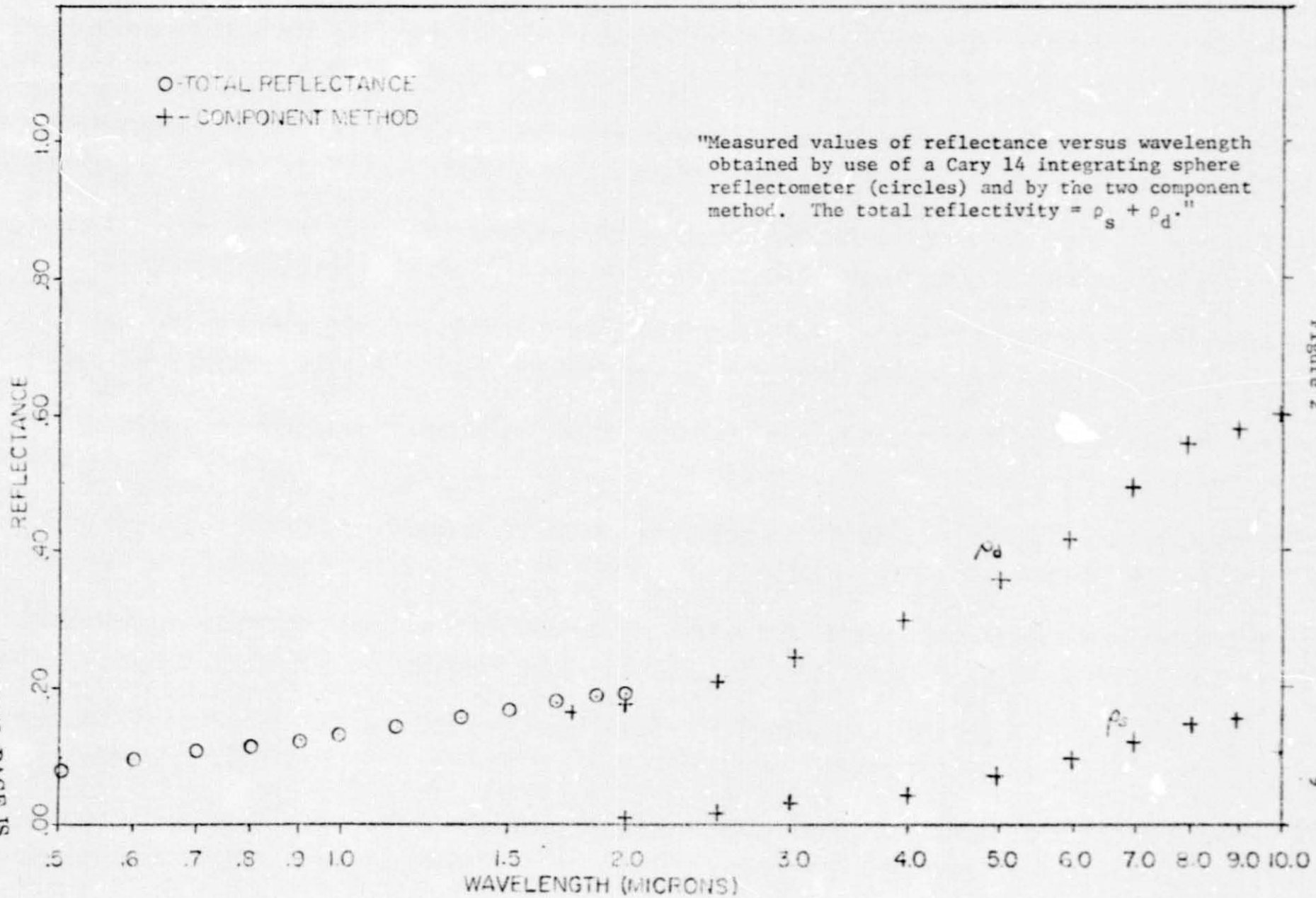


Figure 2

A Selective Surface Suitable for Solar Collectors:

In our first quarterly report we discussed the production of a copper oxide coating which we found to have mildly selective properties. It was produced by immersion of an aluminum alloy with high copper content in an etching solution. The aluminum was removed by the etchant leaving a matrix of oxidized copper. X-ray fluorescence spectra confirmed the presence of copper as the predominant heavy element in the coating although its oxidation state is yet uncertain; presumably it is divalent (i.e., CuO is formed) as can be inferred from its color and relative solubility in nitric acid and ammonium hydroxide. Copper oxides have been found to exhibit selective properties for a copper substrate and an aluminum substrate but have not been exploited extensively because of either difficulty of preparation, expense of substrate, or poor adherence to the substrate. Our technique seems to solve these problems.

Our original effort has extended from several low copper alloys to 2219 (5.3% copper), and has produced coatings with spectral characteristics as shown in Fig. 2. The coating has a fair selectivity and is mainly diffuse. More recently we have explored the effect of substrate heat treatment on coating characteristics. This was motivated by coating morphology studies (done with electron and optical microscopy) which indicate a correlation between substrate grain size and coating particle dimensions. If the particle size could be tailored to somewhat less than the desired cutoff wavelength, the theory of scattering from powders indicated that the coating would be transparent to long wavelength light (with reflectivity characterized by the metallic substrate) but absorbent for short wavelengths. The data shown in Fig. 2 are for a 2219-0 (annealed) sample.

Similar processing of thermally tempered 2219 samples has resulted in qualitatively different coatings. The formation dynamics are not yet understood but we see in this type of coating a very suitable surface for solar collectors with good selectivity and very high absorptivity in the visible part of the spectrum. The coatings obtained on tempered films are sufficiently coherent that uniform interference coloration is observed. After sufficient aging or heat treatment the coatings are comparable to paint in hardness and durability. Although not extensively tested they appear stable at the highest temperatures to be encountered in flat plate collectors; baking at 450°C for three days does not produce undesirable coating changes.

Ellipsometric measurements at 0.63 microns show that for thin coatings the film growth rate in 1N NaOH is 1100 Å/minute for T87 tempered 2219 aluminum at 20°C. Under these conditions the freshly prepared coatings have a real index of refraction, n , of 1.05.

The imaginary part of the index of refraction, k , often called the attenuation coefficient, was 0.1.* Upon baking at 450°C for twenty-four hours the measurements indicated a rise in n to 1.26, a decrease in k to 0.046, and a 20% decrease in coating thickness, presumably representing a compacting of the coating. The coatings produced in 1N NaOH showed rather pale interference colors which changed slightly during the first hour of baking. Further baking for up to three days caused no perceptible change in coating properties.

*In this notation the complete refraction index is $n-ik$.

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Treatment of 2219-TS7 samples in 2N NaOH solutions gave deeper interference colors. We are hence led to believe that the absorptivity (i.e. k) is affected by solution normality while the optical path (i.e. $n \times$ coating thickness) remains constant for a given normality-time product. Baking at 450°C produced a shift in color during the first few hours with no further change over several days. In general the samples were bright-dipped to a fair degree of specularity. Rougher samples (e.g. sandblasted surfaces) produced grayer and presumably less coherent coatings. This is possibly due to uneven film formation so that film interference is averaged out over macroscopic surface areas with subsequent enhancement of absorption by small particle scattering.

Coating colors in 2N NaOH evolved to light straw at 1 minute, light blue at 2 minutes, yellow-green at 3, violet at 4, deep green at 5, deep violet at 6, dark green at 7, very dark purple at 8, with successive interference orders appearing at longer times. These times are approximate and will vary with solution properties, surface pretreatment and temperature of formation. Film darkness increased with etching time until after about 12 minutes the interference colors could no longer be observed. An 18-minute sample was extremely black; measurements at 0.8 microns gave a reflectivity below our threshold (about 1%) for meaningful determinations.

Figure 3 shows a plot of reflectivity versus wavelength for a black chrome sample and one of our CuO samples. We are able to obtain much the same optical properties as the black chrome in the infrared. The visible portion of the spectrum was not explored in this investigation but the greenish appearance of the sample leads us to expect a higher absorptivity

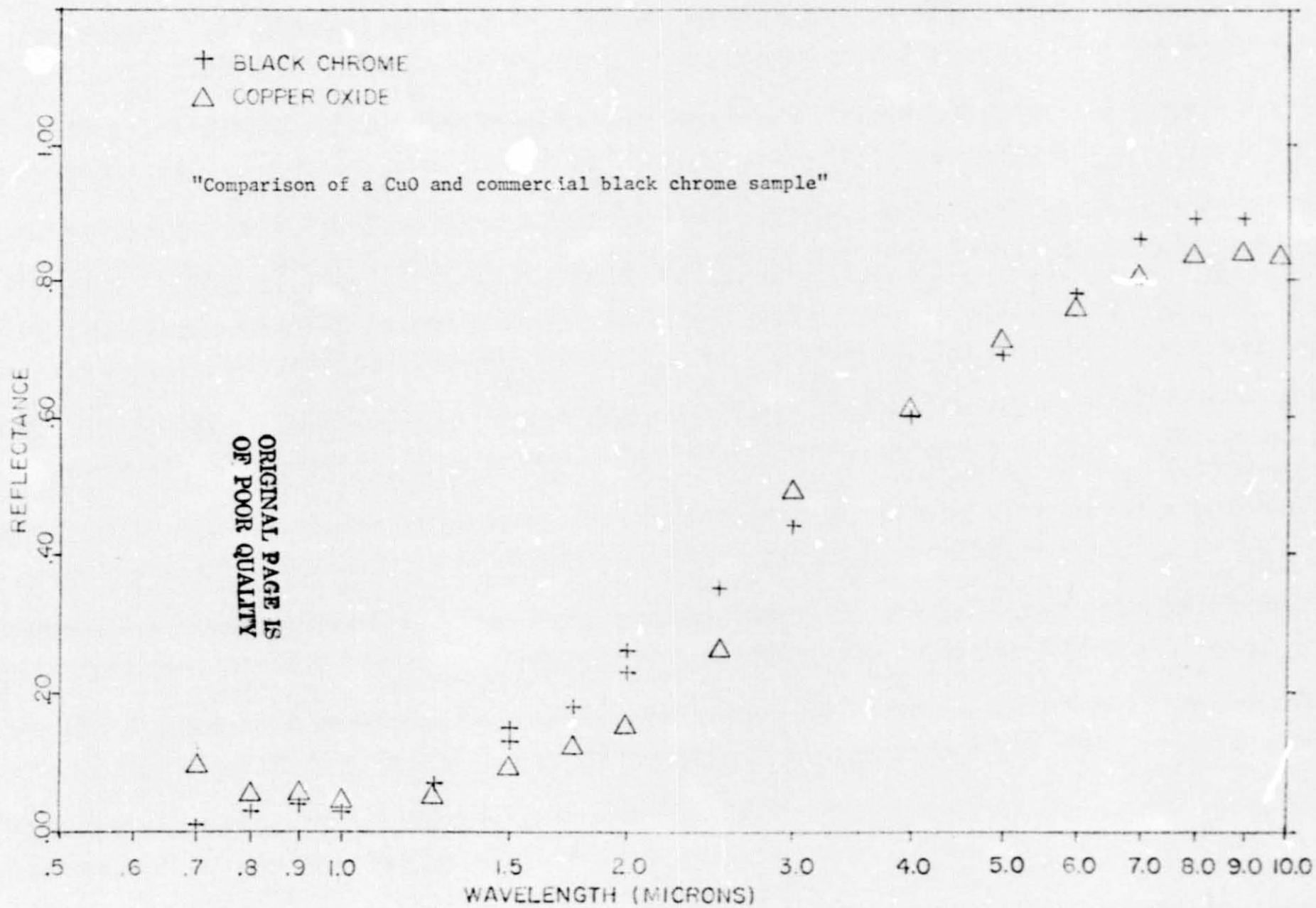


Figure 3

than black chrome in the visible region. Our measurement capabilities in the visible and far infrared are now in the process of being extended. In Fig. 3 the aluminum sample was highly polished before etching.

Figures 4 through 11 show some of the curves obtained for a series of unbaked samples for various treatment times. This data is here presented without extensive comment. We have a theory involving both the optical properties of the coating and interference effects; this work is, however, incomplete and will be included in a future report. The samples were bright dipped so that the surface was fairly specular ($\rho_s \sim 0.8$) although for the small sample size used substrate polish was difficult to control. Coating specularity was determined primarily by initial sample specularity and the long wavelength limit showed a reflectivity equal to that of the untreated aluminum sample. The samples with lower initial polish showed a higher diffuse component of reflectivity. Data in Figs. 4-11 are uncorrected for diffuse reflectivity and represent the specular reflectivity with approximately 20% of the diffuse component added in. Data were reduced through simply dividing the reflected intensity by that for an evaporated gold sample. Taking this factor into account and incorporating other possible errors, we estimate that correction factors in the data would increase the given total reflectance values by up to 25%. Hence nominal long-wavelength limits for the reflectivities are of the order of 0.9, i.e. approximately the reflectivity of the bare aluminum.

Fig. 4 shows a reflectivity curve for an uncoated aluminum sample which had been bright dipped. The variation in reflectivity with wavelength is believed due to a thin coating of copper oxide ($\sim 100 \text{ \AA}$) left on the

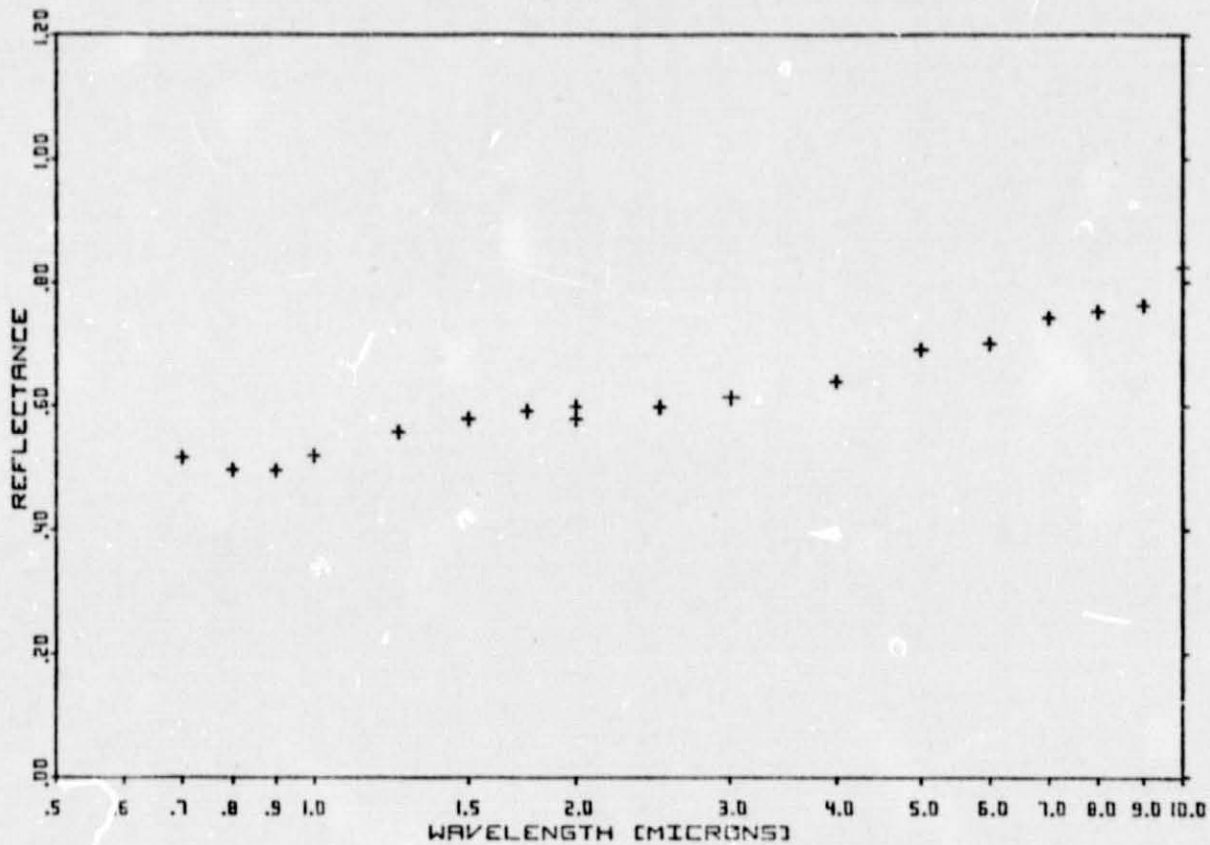


Figure 4

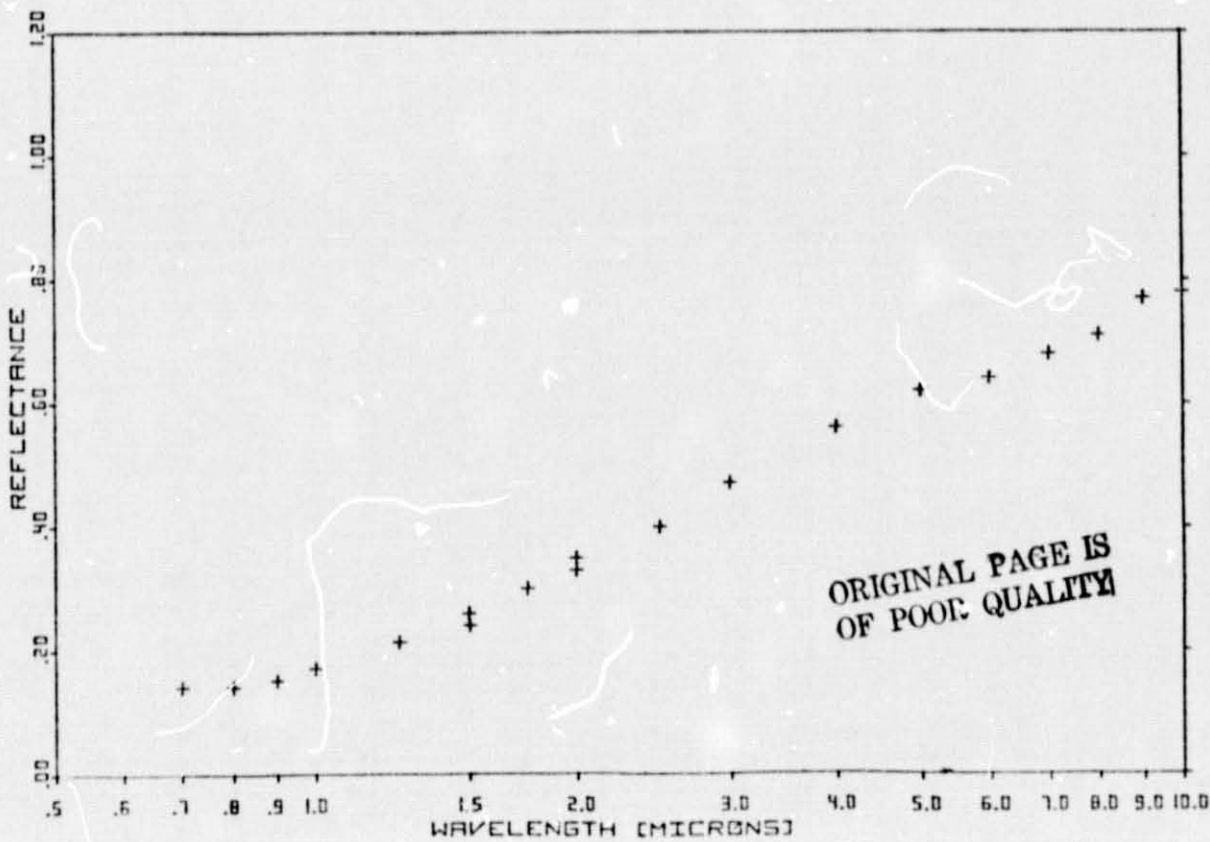


Figure 5

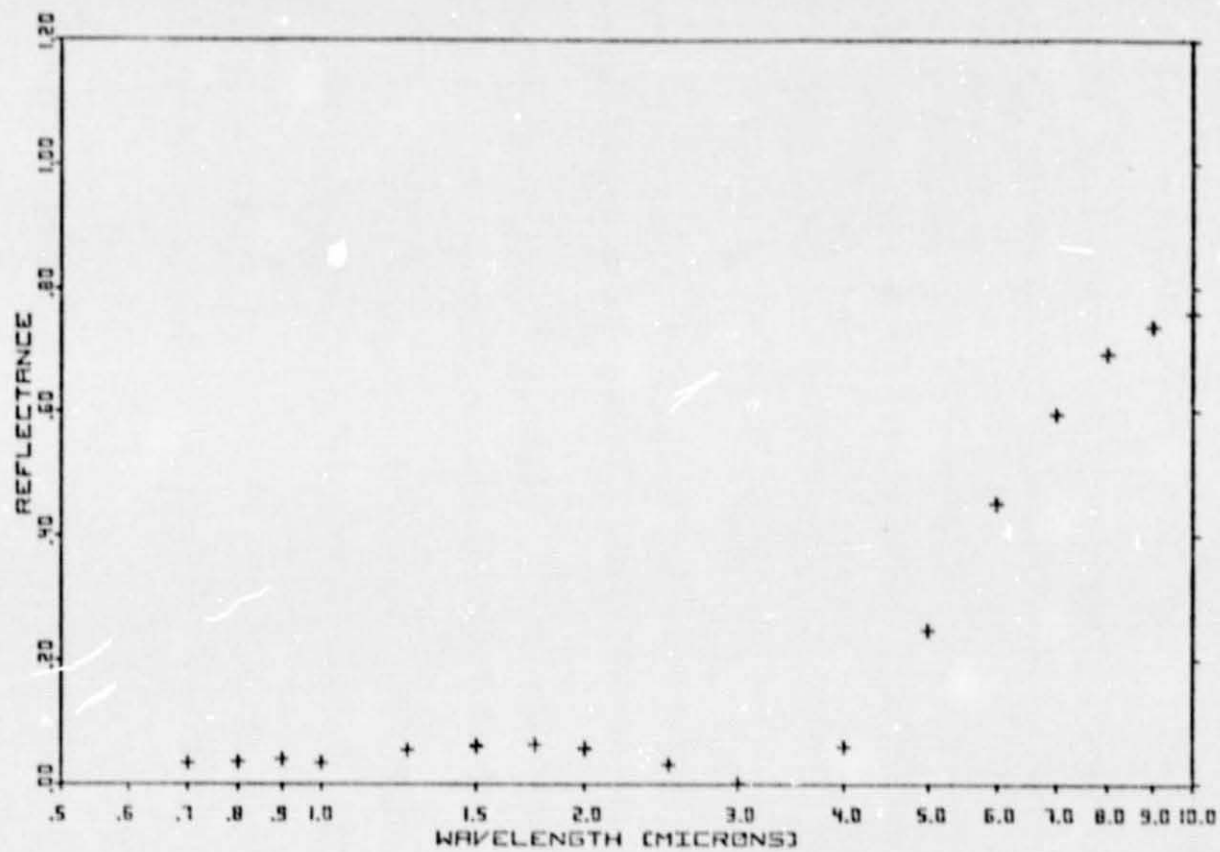


Figure 6

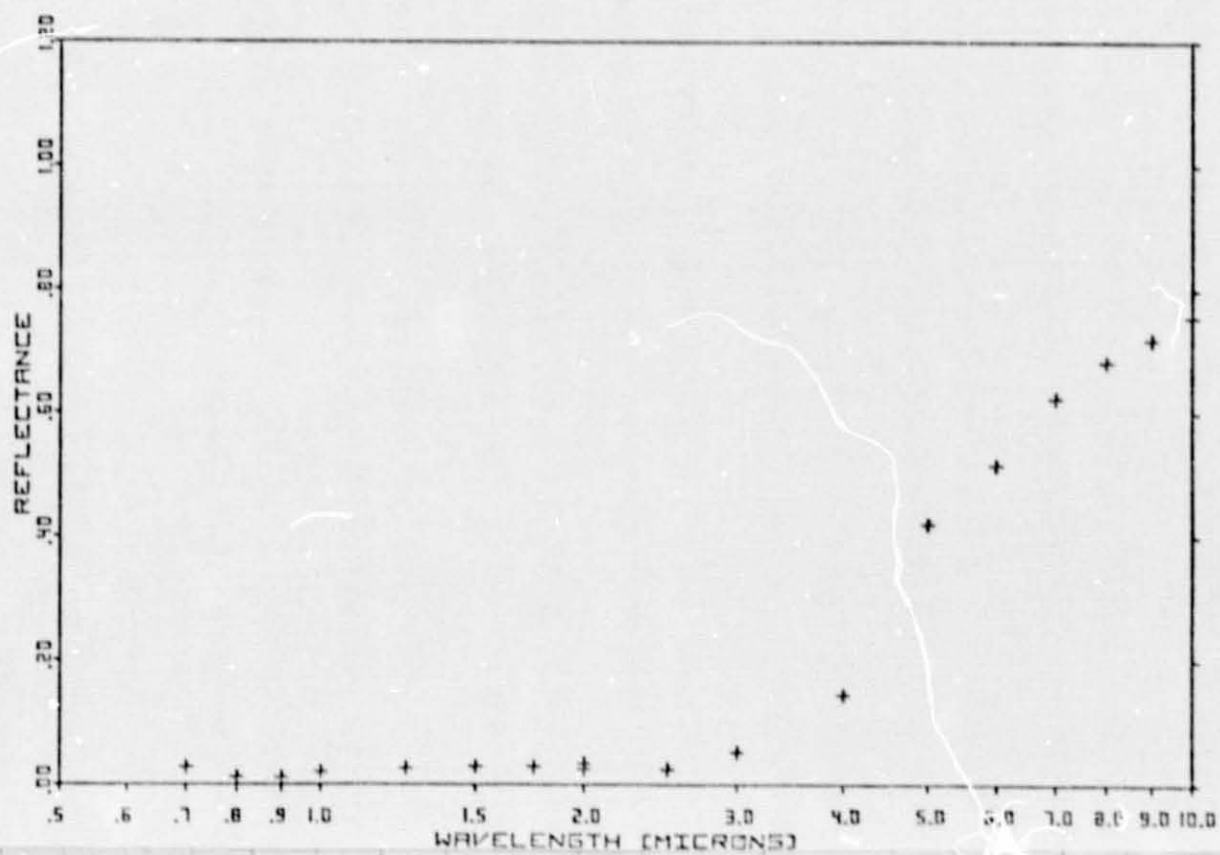


Figure 7

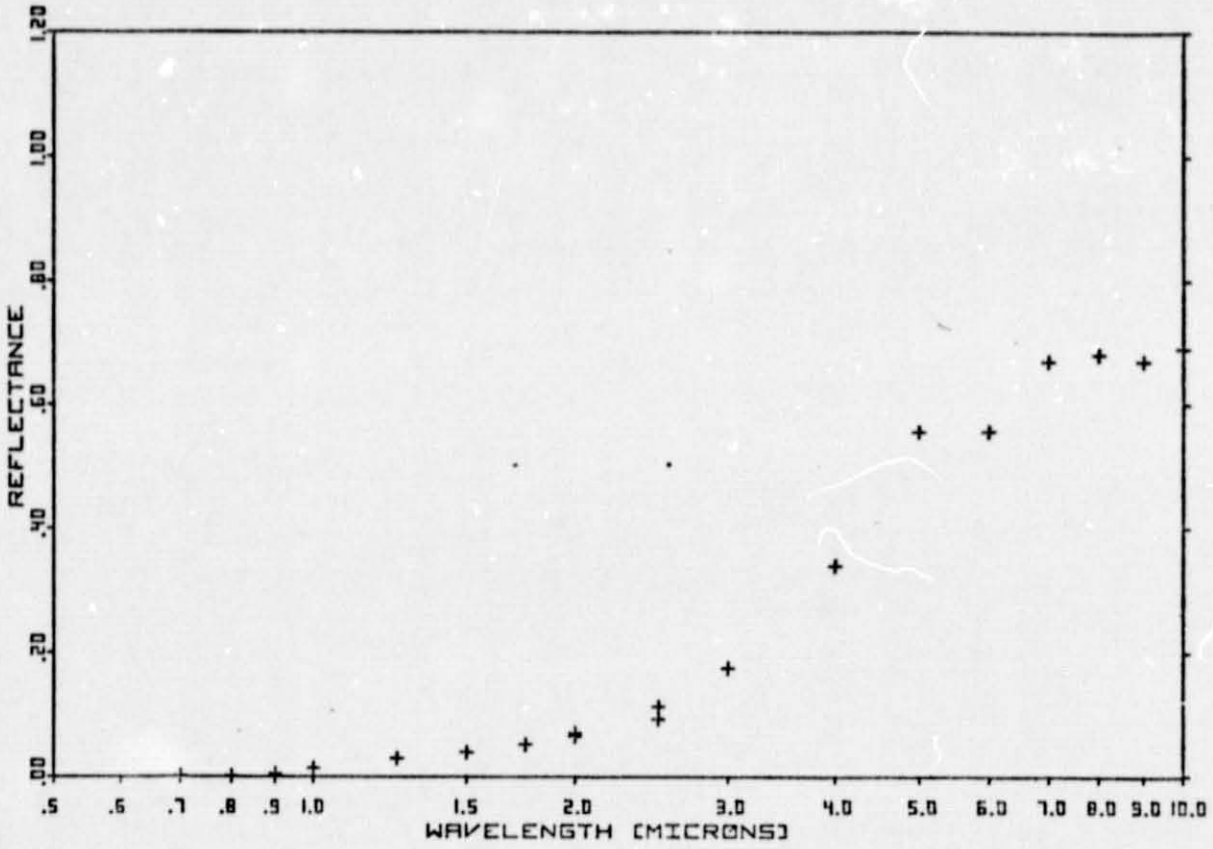


Figure 8

SAMPLE 10

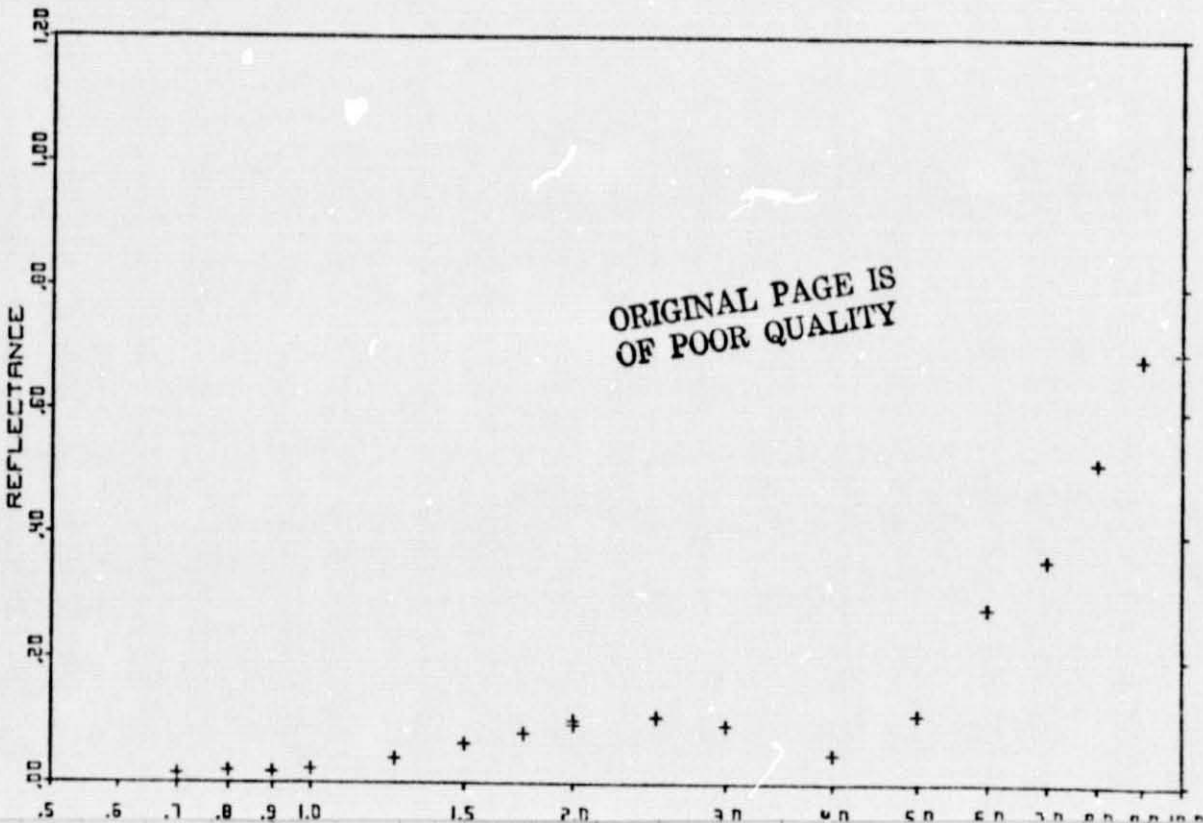


Figure 9

SAMPLE 13

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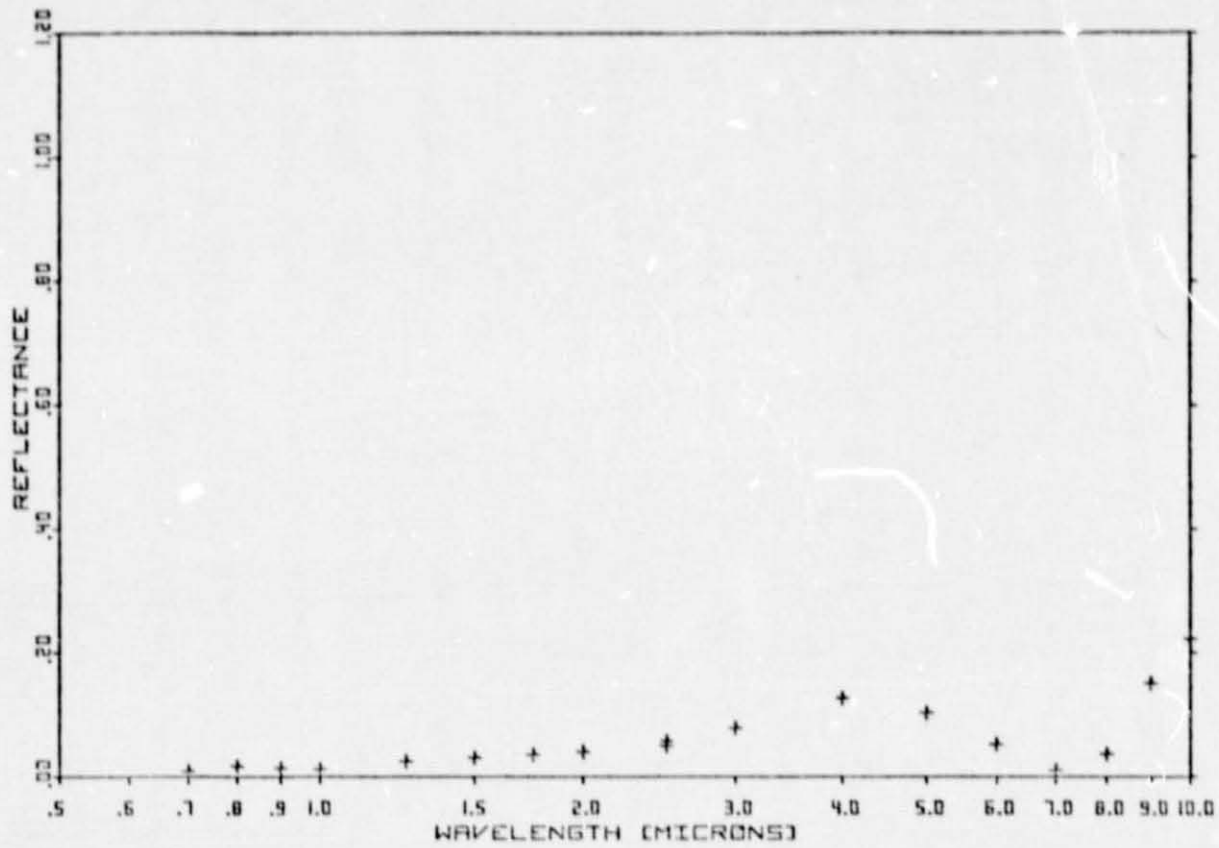


Figure 10

SAMPLE 16

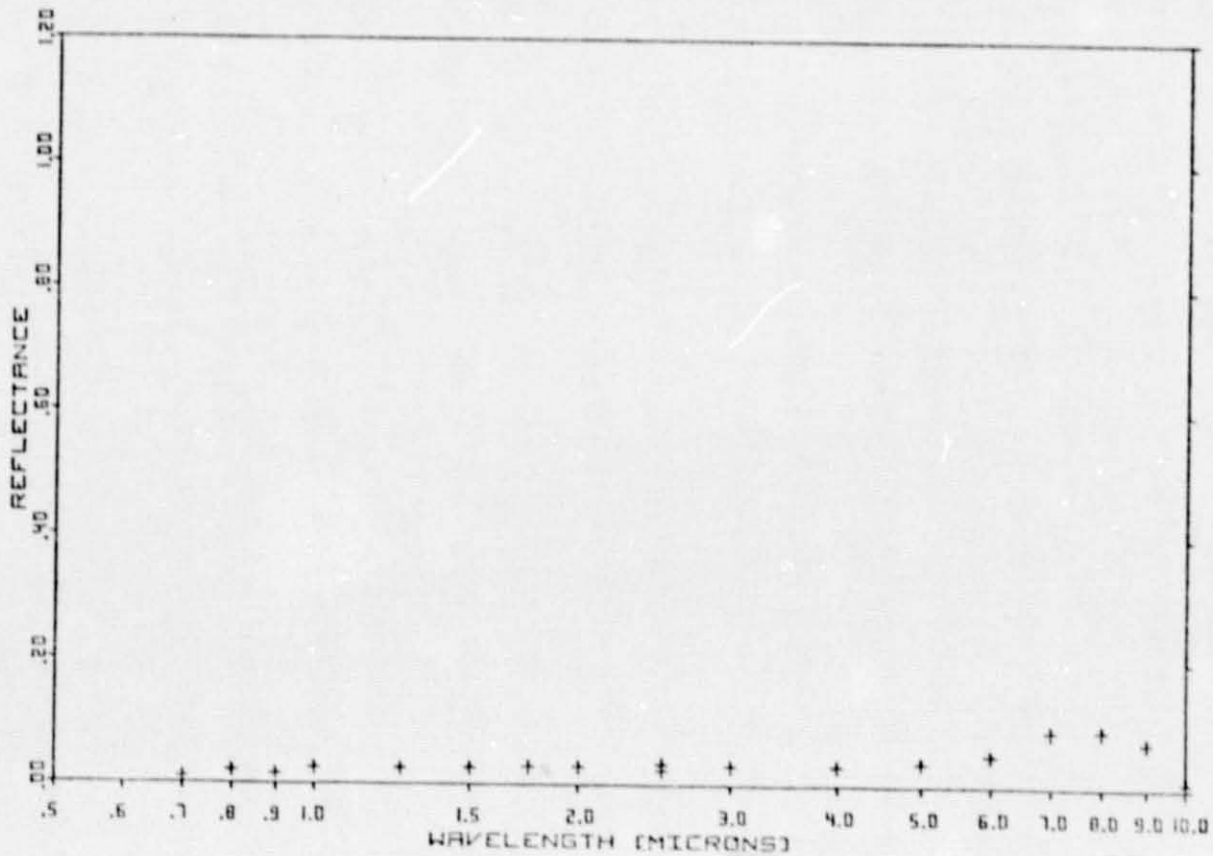


Figure 11

surface. Fig. 5 shows the results for a 2 minute sample which appeared light blue; the reflectivity appears to swing upward in the visible region of the spectrum. Figs. 6 and 7 show a bright yellow-green sample (3 min.) and a green-violet sample (5 min.), respectively. Both of these samples show selectivity but are obviously reflective in regions of the visible. Fig. 8 shows data for a sample (6 min.) we believe to possess excellent selective properties; the sample looks extremely black, by actual measurement has low reflectivity ($< 1\%$) in the near infrared and high reflectivity (after corrections for diffuse reflections - 85-90%) at long wavelengths. Figures 9, 10, and 11 show data for samples treated for 8, 11, and 18 minutes respectively. A general blackening is observed with treatment time with the rise in reflectivity moving toward longer wavelength. The "humps" in the data are believed to be due to interference effects in the coating.

In summary, we have originated methods by which apparently desirable and economical selective absorbing coatings can be fabricated on certain aluminum alloys. They are thermally and physically stable. We are in the process of extending measurements into short wavelength regions so that a better figure of merit for the coating selectivity can be obtained. We have also originated a model to explain the surface selectivity. Samples of the recent surface developments are being sent to our contract monitor, Mr. Roger Linton.

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Considerations for Collector Design:

Several authors¹⁻⁵ have recently reported calculations for the efficiencies of various types of solar energy collectors under varying conditions and with different types of cover plates and absorbing surfaces. While the details of the calculations and considerations differ somewhat, many of the results are in general agreement and are pertinent to some of the objectives of this project.

A schematic diagram of a flat plate collector is shown schematically in Fig. 12. The relevant heat flow parameters are given in the figure where:

Q_T = total incident flux

Q_A = heat absorbed by collecting fluid

Q_a = heat absorbed by absorbing surface

Q_{lr} = heat loss by radiation

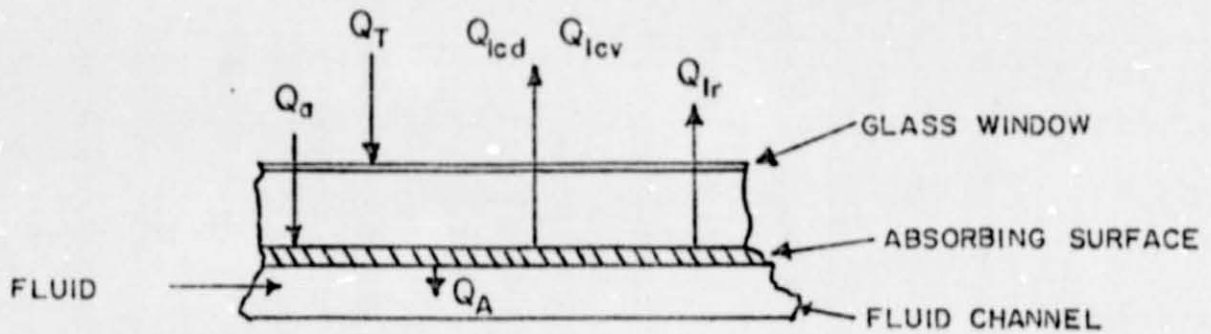
Q_{lcd} = heat loss by conduction

Q_{lcv} = heat loss by convection

This notation follows that given by Ahmadzadeh and Gascoigne¹ (AG). The efficiency of the collector is then defined by

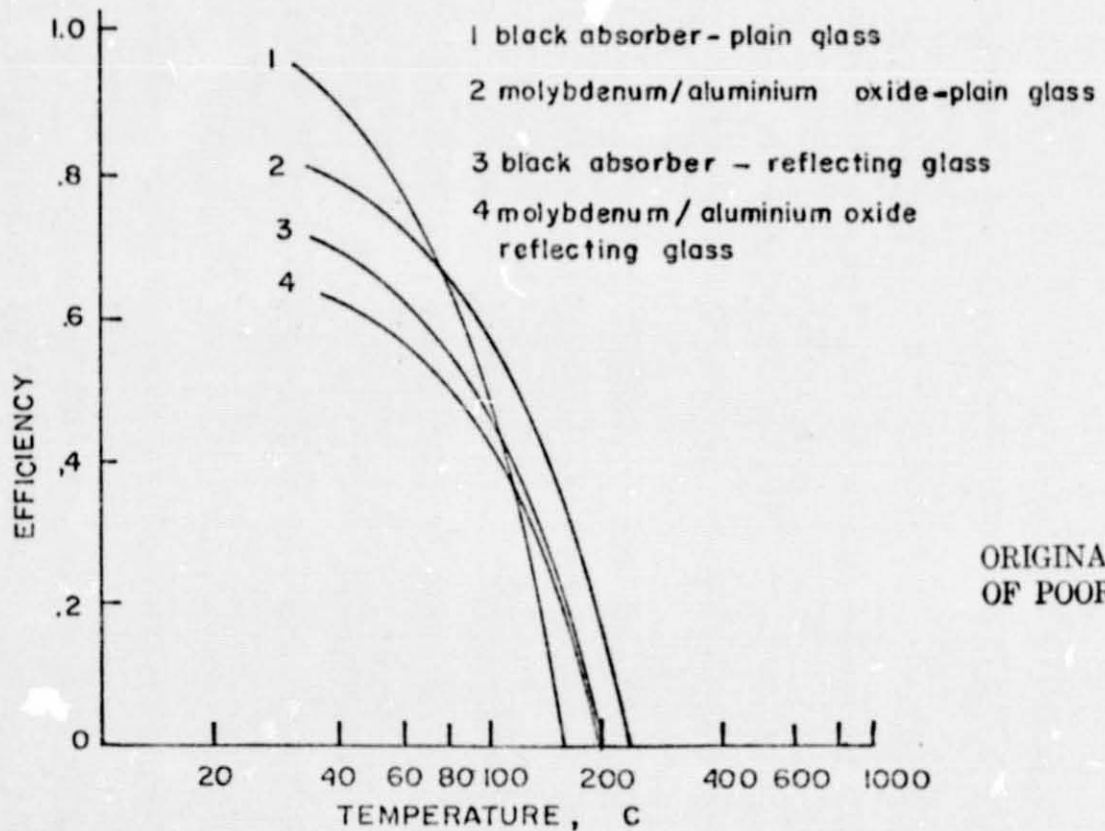
$$\lambda = Q_A / Q_T .$$

The various authors treated the details of the calculation somewhat differently. (AG), for example, found an expression for Q_a in terms of an integral over radiation distributions and absorptivity as a function of wavelength. Young², however, treats the problem in terms of average emissivity. In addition, the boundary conditions for the heat flow problem are handled differently.



FLAT PLATE COLLECTOR

Figure 12 (a)



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Figure 12 (b)

The losses from the flat panel include radiation loss, conduction, and convective losses. The relative amounts of each loss is a function of temperature and the details of the emissive properties. The loss of energy from the absorber to the glass cover plate is dominated at all temperatures by radiation, although convection and conduction play a part. The loss from the glass cover is dominated by convective losses for temperatures 50°C above ambient. The radiation loss is about constant² since the temperature of the cover plate does not depart too far from ambient temperature.

In terms of the parameterization given, the heat absorbed by the collecting fluid is

$$Q_A = Q_a - Q_{lr} - Q_{lcd} - Q_{lcv} .$$

Each of the heat loss terms, Q_{lr} , Q_{lcd} , and Q_{lcv} , can be calculated or estimated with varying degrees of sophistication. The degree of sophistication of these estimates is the primary difference in the model calculations performed. The results of (AG) for a black flat plate collector with a single plain glass window and with a reflecting window is shown in Figure 12b. Also shown are results for a selective surface, with two types of windows, one plain glass window and one coated to be infrared reflecting. At low temperature, i.e. less than 50°C above ambient (assumed to be 20°), the black absorber with a plain window exhibits a higher efficiency than the other models. It is only for temperatures in excess of 70°C that the selective absorber helps. It is further noted that a reflecting window does little good for either case at low temperatures. The results of Young show the same general trend. The solar absorptivity, α , of the surface is the dominant and most important parameter for low temperatures. It is

more important to maintain a high α than to strive for a low infrared emissivity ϵ .

Dolan⁵ experimentally determined the efficiency of a number of collector designs and surfaces both with a solar simulator and in actual solar absorbing conditions. His results suggest the same thing, i.e. for low temperatures maintain a high α for optimal results.

Many of the applications of flat plate collectors will be for space heating and hot water supply where high temperatures will not be realized. For these applications it is probably best to optimize the solar absorptance for maximum efficiency. For similar reasons the use of reflecting cover glass plates needs to be carefully considered. By virtue of their reflectivity in the infrared region of the spectra the plates are somewhat less transparent to the solar radiation. This decreases the energy input to the absorbing plate and affects the overall efficiency. (AG) indicate, in fact, that reflecting coatings are counterproductive in most flat plate applications. If one is using a black absorber at high temperatures where radiation becomes important, it is better to go to a selective surface with plain glass than to add a reflecting glass cover plate to the plain black absorber.

The studies do indicate a need for selective surfaces in concentrating collectors. In these designs when the temperature of the absorber is in excess of 100°C the selective surface can significantly enhance the efficiency of the system.

If these observations concerning flat plate collectors are indeed found to be substantiated by further research, then efforts should be made toward producing durable black surfaces with high solar absorptance. The mechanical and weatherability criteria are then probably of greater importance than selectivity of the surface and should be optimized along with the solar absorptivity for cost effective and consumer attractable systems.

The suggestions and the conclusions of the literature cited in this section will be further evaluated in future reports.

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Future Work:

We will complete work on the improvement and extension of the range of our reflectometry apparatus. Further characterization of our selective surfaces will be accomplished. In particular we will investigate (briefly) surface morphology through electron microscopy and possibly through Auger analysis. We also plan to run (important) humidity tests in order to ascertain coating stability under applied conditions.

Work on materials for selective absorbers is also under way. We are studying etching processes in glass to provide antireflecting surfaces, selective coatings for glass and plastic surfaces and have considered plastic materials with "open" polymeric properties to provide a mesh filter effect.

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3. F. L. Test, Energy Conversion 16, 23 (1976).
4. Rainer Köhne, "Der Flache Sonnenkollektor Energiebilanz und Wirkungsgrad," DLR-FB 75-3. Sponsored by Deutsche Forschungs und Versuchsanstalt für Luft und Raumfahrt.
5. F. J. Dolan, "A performance evaluation of various coatings, substrate materials and solar collector systems," NASA-TM-X-73355, Sept. 1976.

B. Current Problems Impeding Performance

All problems were technical in nature. The speed and quality of the reflectometry data could be enhanced by obtaining a large surface area detector. This would increase the amount of reflected beam intercepted and hence increase the sensitivity of the measurements.

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C. Financial Statement

The major portion of the funds of this contract have been expended, i.e. about \$27,950. The major expenses of the contract were summer salaries for the principal investigators, ~ \$15,600, and about \$10,760 in overhead money. Remaining are \$403 in travel funds and \$220 in expendable equipment funds.