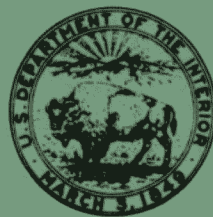UNITED STATES
DEPARTMENT OF THE INTERIOR

PRODUCING SELECTIVELY INFRARED-REFLECTING SURFACES ON PLASTIC FILMS FOR SOLAR STILLS

OFFICE OF SALINE WATER

RESEARCH AND DEVELOPMENT PROGRESS REPORT NO. 53

UNITED STATES
DEPARTMENT OF THE INTERIOR

Stewart L. Udall, Secretary

Kenneth Holum, Assistant Secretary
For Water and Power Development

SALINE WATER RESEARCH AND DEVELOPMENT PROGRESS REPORT NO. 53

PRODUCING SELECTIVELY INFRARED-REFLECTING SURFACES
ON PLASTIC FILMS FOR SOLAR STILLS

BY

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FOR

OFFICE OF SALINE WATER

FOREWORD

This is the fifty third of a series of reports designed to present accounts of progress on saline water conversion with the expectation that the exchange of such data will contribute to the long-range development of economical processes applicable to large-scale, low-cost demineralization of sea or other saline water.

Except for minor editing, the data herein are as contained in a final report submitted by The Franklin Institute, Laboratories of Research and Development under Contract No. 14-01-001-206 covering research carried out from June 1, 1960 to July 31, 1961. Robert A. Erb, Project Engineer, was in charge of the research; Edmund Thelen, Manager, Colloids and Polymers Laboratory and F. L. Jackson, Assistant Director of the Laboratories were responsible for general supervision of the project for Franklin Institute. The data and conclusions given in this report are essentially those of the contractor and are not necessarily endorsed by the Department of the Interior.

ABSTRACT

Basic considerations of radiant energy behavior in solar still systems are discussed with conclusions presented as to the limitations of still design on the use of selectively infrared-reflecting coatings. Two classes of infrared coatings are discussed: thin metal films, and interference reflection filters (single and multiple-film types). The overall conclusions presented are that the metal film approach is technically infeasible (will not conserve energy), and that the interference coating approach is technically feasible but economically infeasible.

1. NATURE OF THE PROBLEM

Aside from lowering operating costs, there are two basic ways of lowering the cost of produced water from a solar still. One is to lower the effective cost per unit area of the still and the other is to increase the efficiency of the still; that is, to increase the water output per unit area of the still. These two approaches, of course, must be considered together, as still cost per unit area might go up as efficiency goes up with some design changes, thereby negating some or all of the decrease in produced water cost. This program of study has been directed at investigating the feasibility of increasing solar still efficiency by the use of selectively infrared-reflecting surfaces on the solar-transparent cover.

By "selectively infrared-reflecting" is meant that the coating or surface treatment will be substantially transparent (low absorbance and reflectance) to solar radiation in the visible and near infrared wavelengths but be highly reflective to the bath re-emitted radiation, which peaks in intensity in the $9\text{-}10\ \mu$ region. It is of some note that there is very little literature concerned with selectively reflecting films specifically for solar and ambient-re-emitted wavelengths. This is in contrast to the abundance of literature on selectively absorbing surfaces which have a high absorptivity (almost ideal blackbody behavior) for solar wavelengths but a low emissivity for the re-emitted wavelengths.

The thought behind this project was to provide means for preventing radiant heat losses from the bath to the roof with subsequent dissipation from there. The greenhouse effect which occurs when an enclosure covering is transparent to solar wavelengths but is opaque (i.e., highly absorptive) to re-emitted radiation, could be enhanced if the re-emitted radiation were reflected rather than absorbed by the cover.

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Early in this program the following topics were studied; (1) the nature of the re-emitted radiation from the bath and incident solar radiation; (2) the optical behavior of thin water films toward the re-emitted radiation; (3) applications of these considerations in still designs utilizing selectively infrared-reflecting coatings.

The first consideration is of the nature of the radiant energy re-emitted from the bath. In the wavelength region under consideration water, both saline and fresh, behaves approximately as a blackbody. The wavelength at which the spectral emittance (radiant emittance per unit range of wavelength) of the blackbody is a maximum for a specified temperature is given by an equation which follows from Wein's displacement law. The equation is:

$$\lambda_{max} \, T = 2.897 \times 10^3$$

where λ_{max} is the wavelength in microns and T is the absolute temperature in degrees Kelvin. Figure 1 is a plot of calculated values of λ_{max} vs temperature over the range of temperature that might be found in basin water involved in solar distillation processes (i.e., from about 20° - 70°C). It is of some note that λ_{max} does not vary appreciably, only from about 9.9 to 8.4 microns, as the temperature goes from 20° to 70°C. This fact is of some importance in any work with quarter-wave "tuned" reflecting films for operation over a range of temperatures.

The radiant emittance of a blackbody is a function of the absolute temperature to the fourth power, and is given by the Stefan-Boltzmann equation:

$$W = 5.672 \times 10^{-8} \, T^4$$

where W is the radiant emittance in watts/m^2 and T is the temperature in degrees Kelvin. Figure 2 is a plot of radiant emittance vs temperature over the range of typical basin temperature.
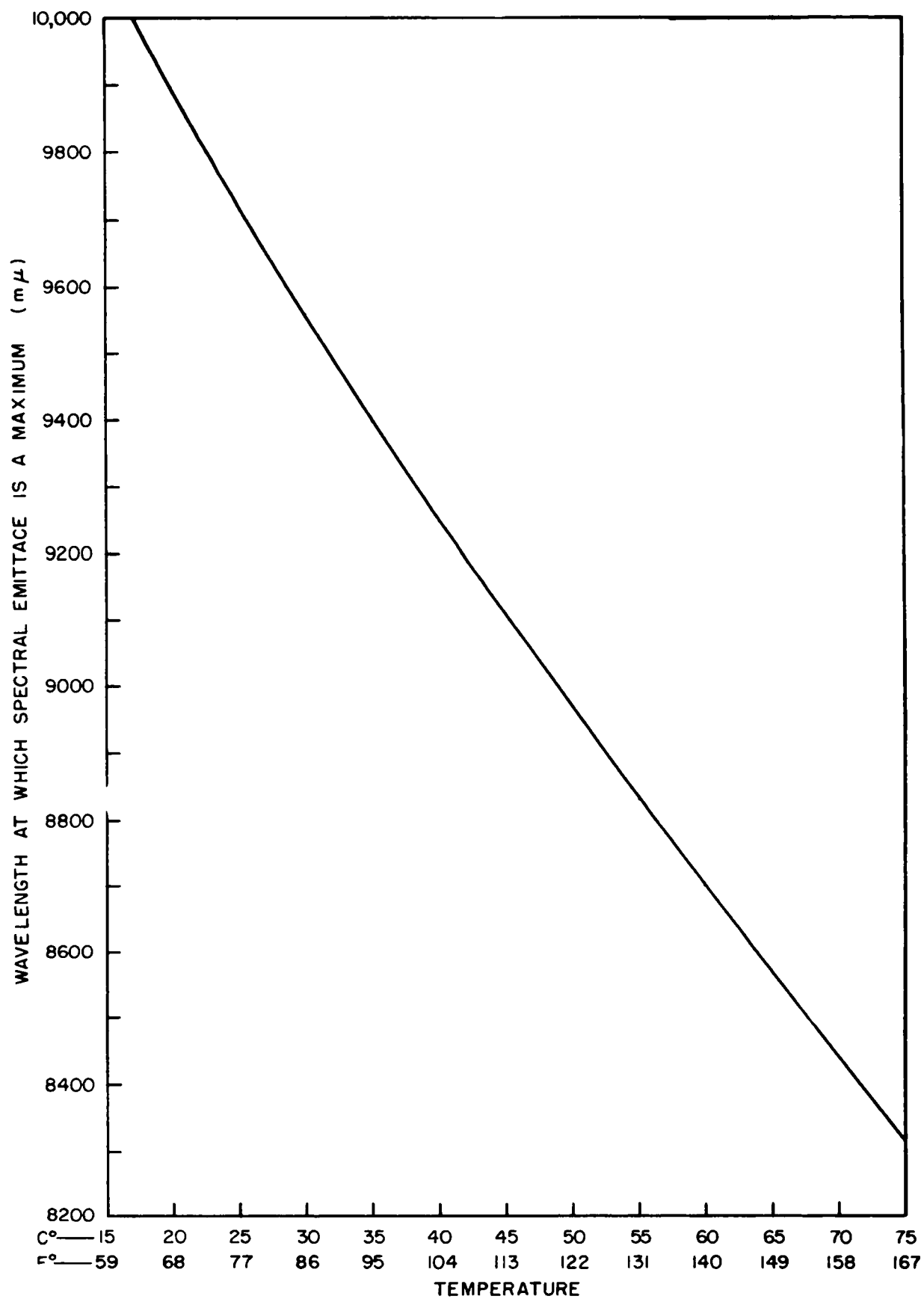
FIG. I. WAVELENGTH AT WHICH SPECTRAL EMITTANCE IS A MAXIMUM vs TEMPERATURE, CALCULATED FOR SOLAR STILL TEMPERATURES FROM WIEN'S DISPLACEMENT LAW
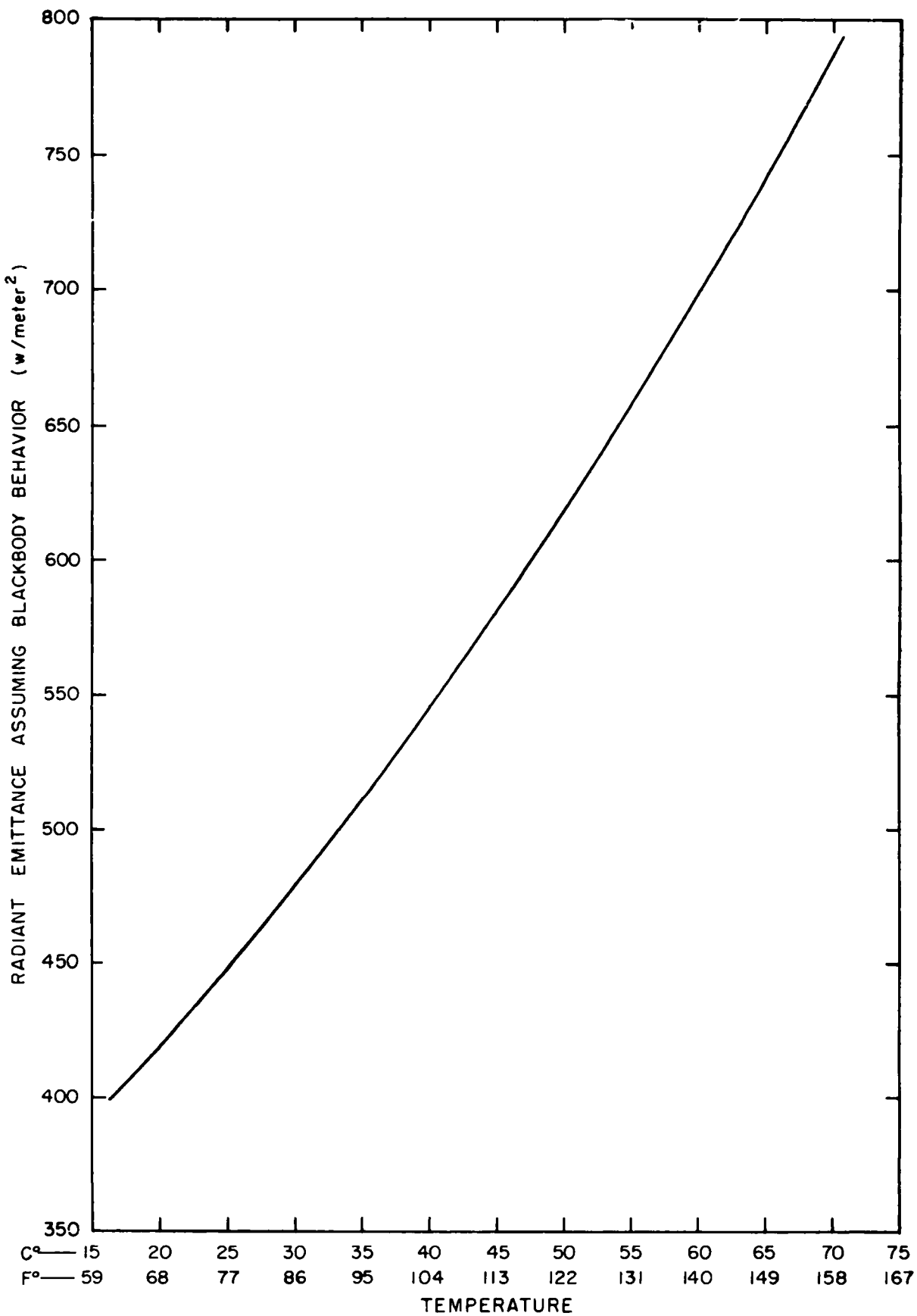
FIG 2. RADIANT EMITTANCE FOR A BLACKBODY vs. TEMPERATURE, CALCULATED
FOR SOLAR STILL TEMPERATURES FROM THE STEFAN-BOLTZMANN LAW

The radiant emittance is affected more strongly by temperature change than is λ_{max} because of the exponential term. Over the range from 15° to 70°C the radiant emittance from a water bath approximately doubles (from 400 watts/m^2 to 800 watts/m^2).

The spectral emittance of a blackbody can be obtained in terms of temperature and wavelength by the following equation:

$$W_\lambda = \frac{C_1 \lambda^{-5}}{\varepsilon^{C_2/\lambda T} - 1}$$

where W_λ is the spectral emittance, λ is the wavelength, T is the Kelvin temperature, ε is the base of natural logarithms, and C_1 and C_2 are constants. When W_λ is in watts/m^2 - mμ and λ is in mμ, $C_1 = 3.740$ x 10^{20} and $C_2 = 1.4385$ x 10^7. Figure 3 was plotted from a series of W_λ and λ values calculated for a blackbody at 40°C (104°F, 313.2°K). This is a typical figure in the range of typical evaporating basin temperatures. The area under such a curve of spectral emittance vs. wavelength is numerically equal to the radiant emittance when consistent units are used.

Figure 4 is a plot on the same graph of spectral emittance of a blackbody at 40°C and of the approximate maximum spectral solar irradiance (incident solar power per unit area, per unit range of wavelengths) on a horizontal surface at sea level in temperate latitudes in midsummer, both vs. wavelength. Linear scales on the ordinate and abscissa are used so that the area under the curves is a direct measure of the incident or emitted radiant flux per unit area. Note the strong difference in the shape of the two curves. There is an extremely small area overlap of the two curves (so small that it cannot be seen on a graph of this scale); this is favorable in that a reflection filter with a sharp cutoff in the 3-4 μ range could pass effectively 100% of the incident solar radiation, yet reflect 100% of the radiation emitted from a bath at 40°C or thereabouts. The difference in the shapes and
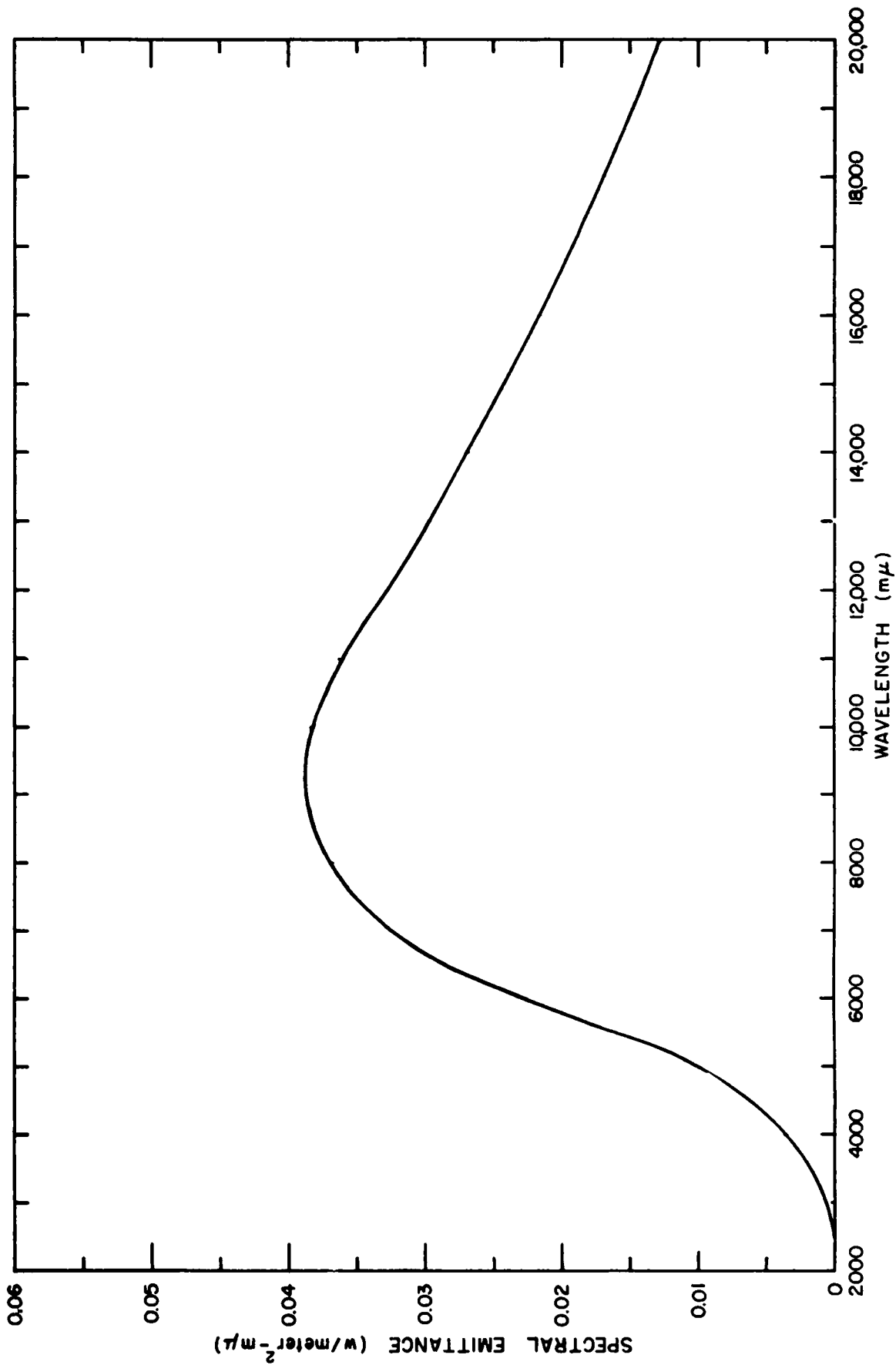
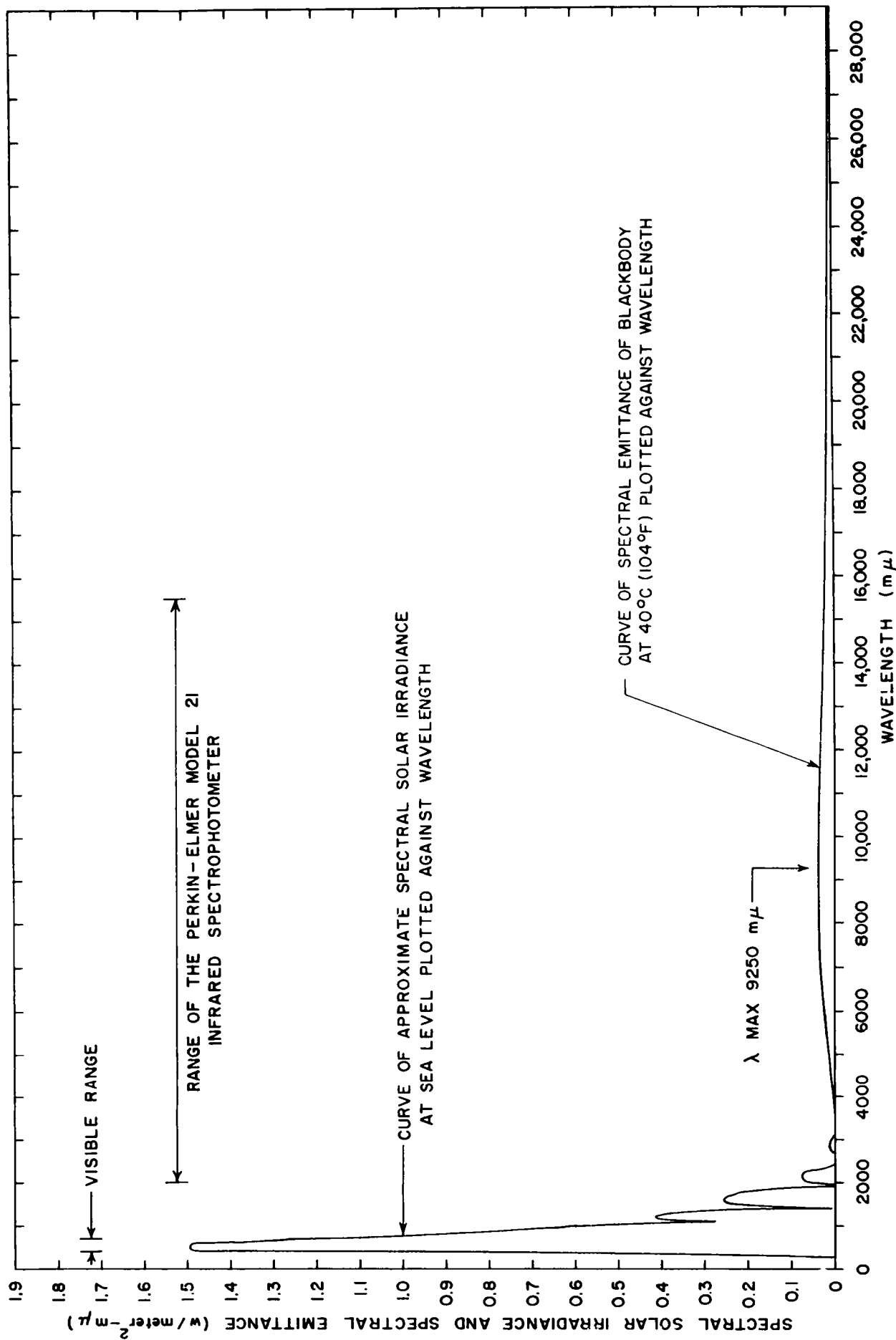FIG. 3. SPECTRAL EMITTANCE OF A BLACKBODY AT 40°C vs. WAVELENGTH

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FIG. 4. SPECTRAL SOLAR IRRADIANCE AND SPECTRAL EMITTANCE OF A BLACKBODY AT 40°C vs. WAVELENGTH

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placements of the two curves is due to the fact that the solar curve is essentially that of a blackbody at 6000°K (modified by atmospheric absorption in the visible and UV regions and by selected water and CO_2 absorption bands in the IR region) whereas the water bath is emitting at only about 313°K.

The second topic considered in some detail was the behavior of thin water films toward incident radient energy, particularly for the re-emitted wavelength regions. Qualitatively, water has substantially blackbody behavior for 10 μ radiation (see Dorsey (1), p. 339). For the very thin films such as produced by condensation on solar still covers, a quantitative treatment was included in our study. Figure 5 is a plot of the absorption coefficient of water vs. the wavelength of incident radiation. The data for the 0.7 to 2.5 μ region were obtained from Curcio and Petty (2) and for the visible and remaining infrared region from Dorsey's compilation (1) for a number of investigators. The absorption coefficient, α, is defined by the equation

$$I = I_o \varepsilon^{-\alpha x}$$

where I_o is the initial intensity of the radiation, I is the intensity of the radiation after passing through a layer of the substance x cm in thickness, and ε is the base of natural logarithms. The units of α here are reciprocal centimeters. The general rise of the absorption coefficient with increased wavelength is of note. The absorption coefficient varies through more than five decades with the overall minimum value being at about 0.5 μ in the visible region and the overall maximum at about 15 - 16 μ in the infrared region. The value of the absorption coefficient at 9.25 μ, which is λ_{max} for a blackbody at 40°C, is approximately 690 cm^{-1}. Using this figure we calculated a series of values of spectral transmission, T, (T = I/I_o) for various water film thicknesses.
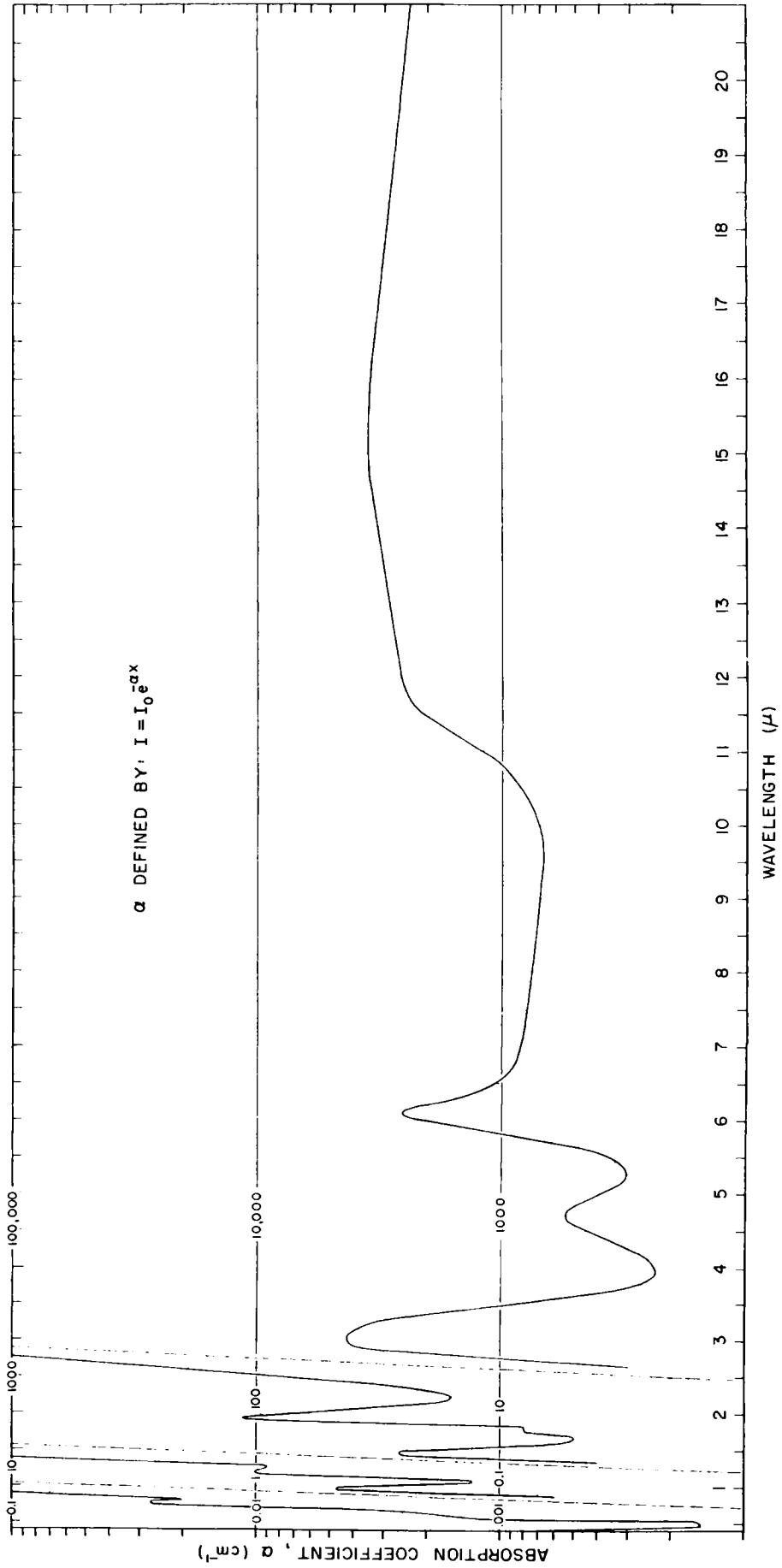
FIG 5. ABSORPTION COEFFICIENT OF WATER vs. WAVELENGTH OF INCIDENT RADIATION

α DEFINED BY: $I = I_0 e^{-\alpha x}$

WAVELENGTH (μ)

ABSORPTION COEFFICIENT, α (cm^{-1})

Figure 6 is a plot of spectral transmission vs. thickness of water film for IR-radiation at 9.25 μ. This gives a direct quantitative measure of IR transmission and absorption. It can be seen that any water film thicker than 35 μ will absorb more than 90% of the re-emitted IR energy. The spectral transmission drops off rapidly above this thickness and for a film 0.017 cm (170 μ) thick only 0.001% of the radiation is transmitted.

A rough calculation was made to determine the order of magnitude of the water film thickness on the inside of the transparent condensing surface in a greenhouse type still. In this calculation the following assumptions were made: (a) the angle of the plane covers is 30°; (b) the width of the still is 6 feet; (c) uniform condensation takes place, and a point half-way down on the surface is being studied; (d) one pound (453.6g) of water is recovered per day for each square foot of evaporating basin; (e) the rate of production is averaged over a 10 hour day; (f) the mean drain rate of the water film at the halfway point is 4 cm/minute. Using these assumptions, the mean water film thickness is 0.0109 cm or 109 μ. From Figure 6 we see that only 0.06% of the re-emitted IR radiation would be transmitted. Thus blackbody behavior is essentially complete from absorption considerations of the condensed water film.

The question of the role of reflection from the water surface also comes up in the discussion of behavior of the films toward radiant energy. Reflection is dependent on the wavelength and angle of incidence of the impinging radiation. Figure 7 is a plot of reflectivity (ratio of reflected to incident radiation intensity) vs. wavelength for radiation of 0° and 50° angles of incidence. The data were obtained from Dorsey's compilation (1). It is noted that for λ_{max} the reflectivities for normal and 50° incident radiation are only about 1.4% and 2.4% respectively - not very large from the heat conservation viewpoint. At about 20 μ the reflectivities are increasing to the 10-15% range; however, very little of the re-emitted energy lies above this region. It is safe to say in
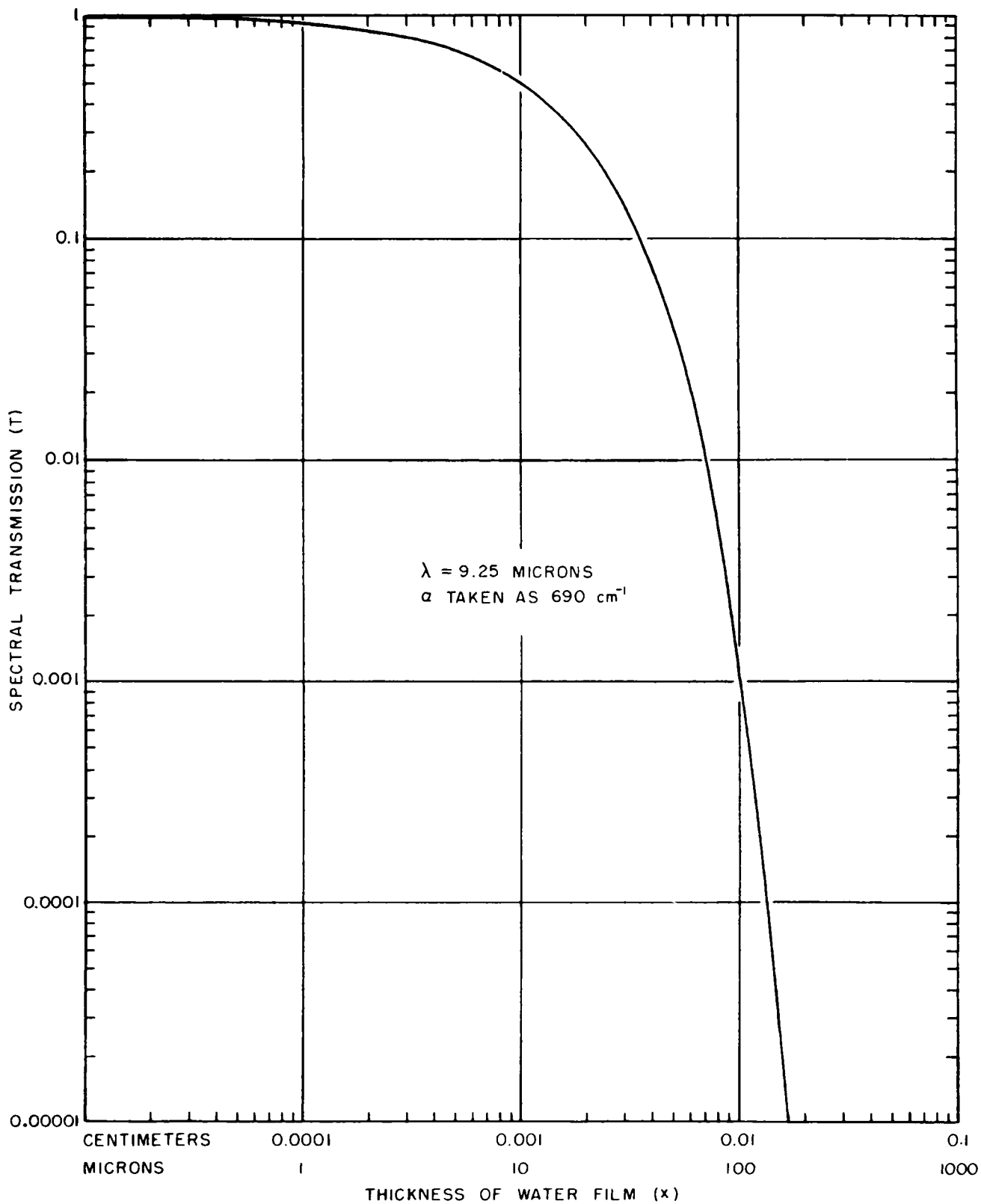
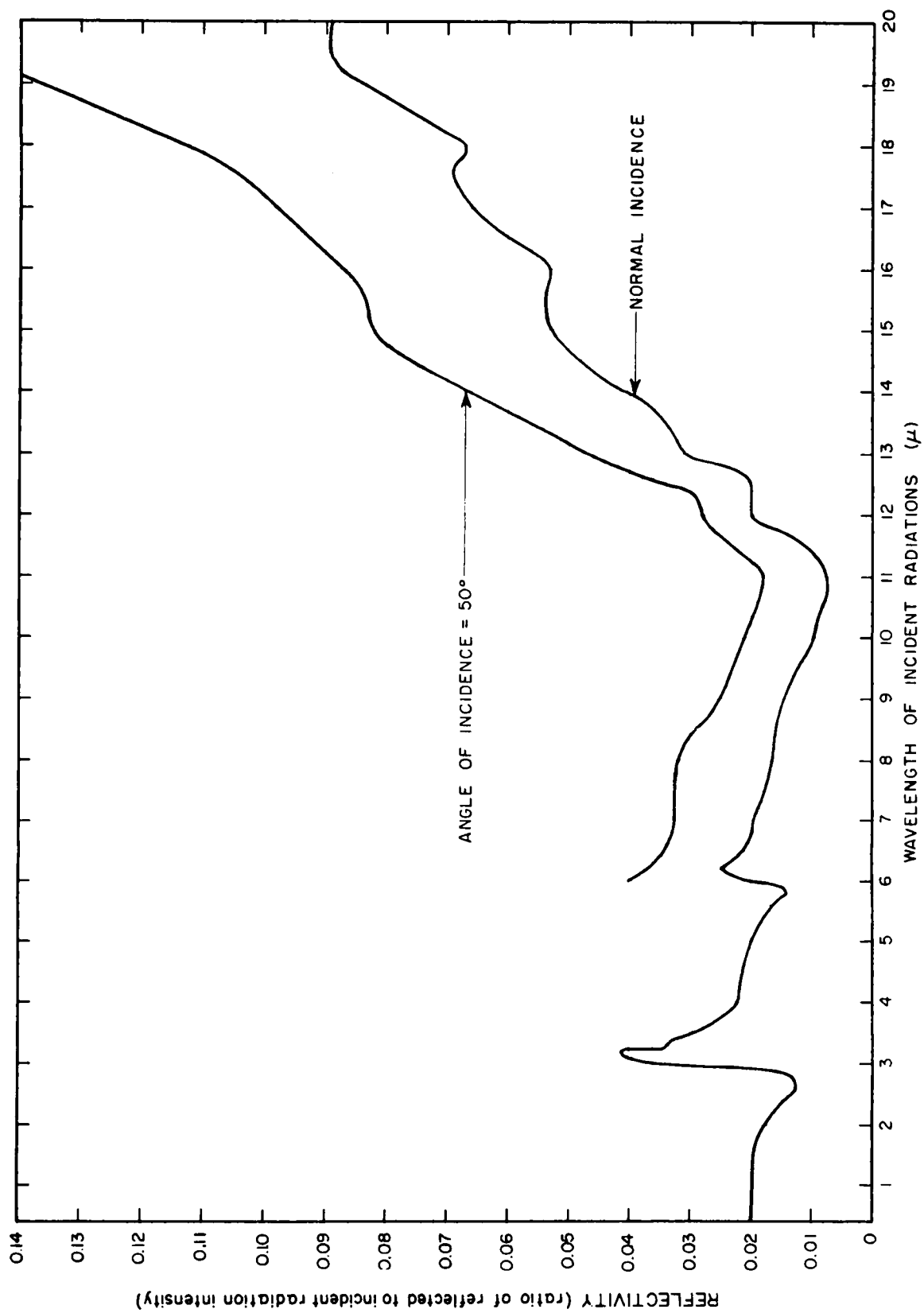FIG.6 SPECTRAL TRANSMISSION vs. THICKNESS OF A WATER FILM (λ = 9.25μ)

FIG. 7. REFLECTIVITY vs. WAVELENGTH FOR WATER FILMS

summary that reflection from water films cause only slight deviation
from their blackbody behavior. A conclusion of this quantitative study
of water film behavior toward incident radiation as emitted from solar
still basins is that absorption occurs with all but a few percent of the
incident energy.

The above information is c great importance in consideration of
solar still designs incorporating selectively infrared-reflecting coatings.
Referring to Figure 8, Arrangement A represents the simple configuration
of a horizontal basin, roof-type solar still in which the transparent
covering also serves as a condensing surface. In the simplest conception
with this system the infrared-reflecting surface is deposited on the
inner surface of the covering to reflect the radiant energy emitted from
the basin back to the basin. This will not work, however. This is
because the water film on the condensing surface has substantially black-
body behavior, as was discussed in the previous section, thereby absorbing
the infrared radiation before it reaches the reflecting surface. Such
absorbed heat is readily transferred by simple conduction across the
reflective film to the cover and dissipated from there in part to the outside
by conduction, convection and radiation mechanisms. Also a portion is
retained in the condensed water. Thus in the simplest case the reflecting
coatings are not useful at all.

Arrangement B represents a similar construction but with the
IR-reflecting surface on the outside. Of particular interest in this
case would be coatings of low emissivity (numerically equal to absorptivity)
in the 6-16 μ wavelength region. Here again the condensed water film
would absorb the re-emitted radiation with resulting removal from the
system by various mechanisms. The low-emissivity coating would reduce
heat loss by only one of these mechanisms, namely, radiation. It would
thus enhance the "greenhouse effect", but only slightly. The final
distillation rate improvement would be reduced by two factors: (1)
increased temperature of the condensing surface; (2) any reduction in solar
transmission caused by the low-emissivity coating. Thus the expected net

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CONDENSED
WATER FILM

INNER IR
REFLECTIVE
SURFACE

ARRANGEMENT (A)

CONDENSED
WATER FILM

OUTER IR
REFLECTIVE
SURFACE

ARRANGEMENT (B)

HOT SALINE WATER OUT

OUTER IR
REFLECTIVE
SURFACE

CONDENSED
WATER FILM

COOL SALINE
WATER IN

ARRANGEMENT (C)

BLOWN AIR TO
OUTSIDE CONDENSER

NO CONDENSED
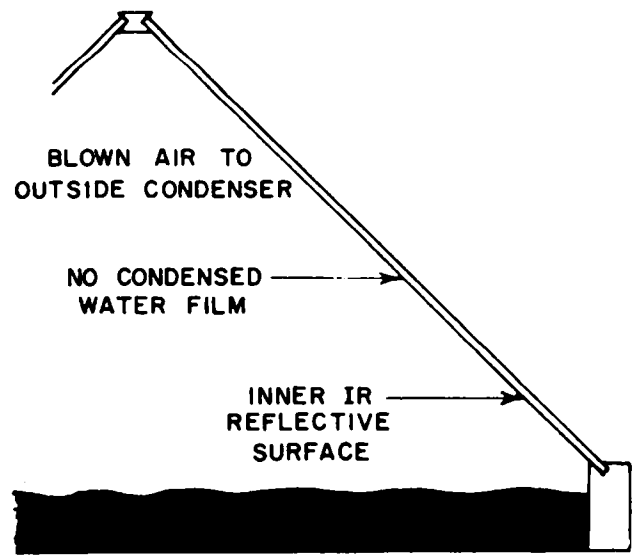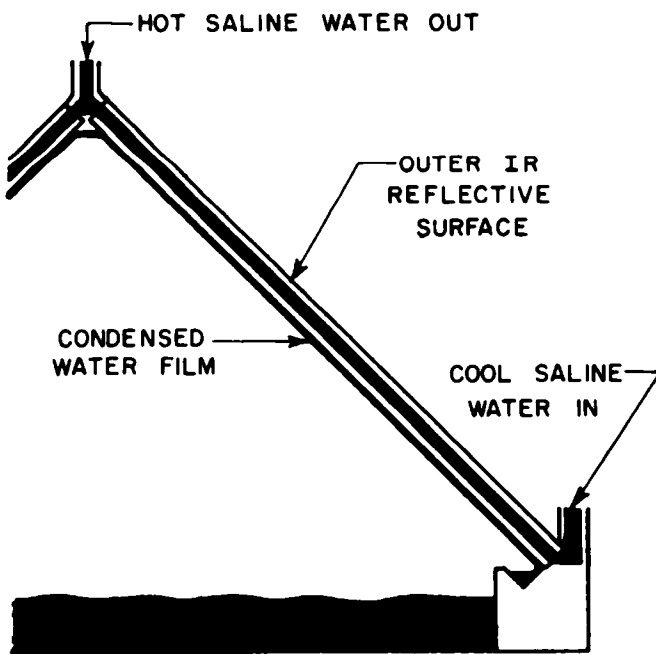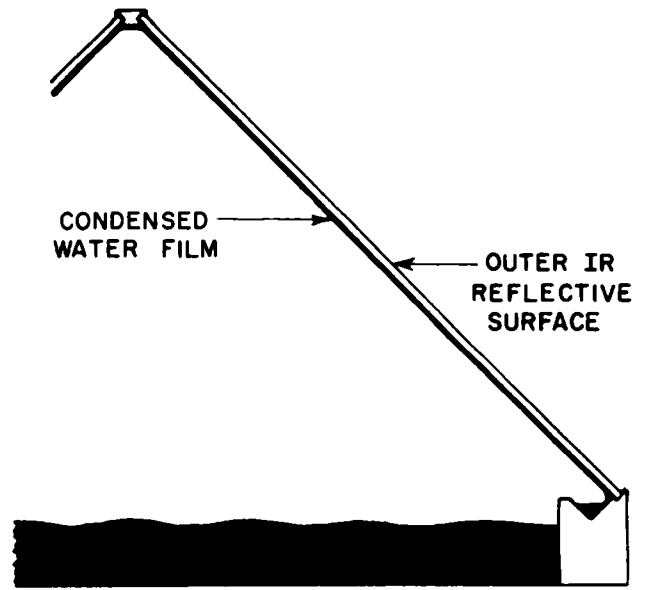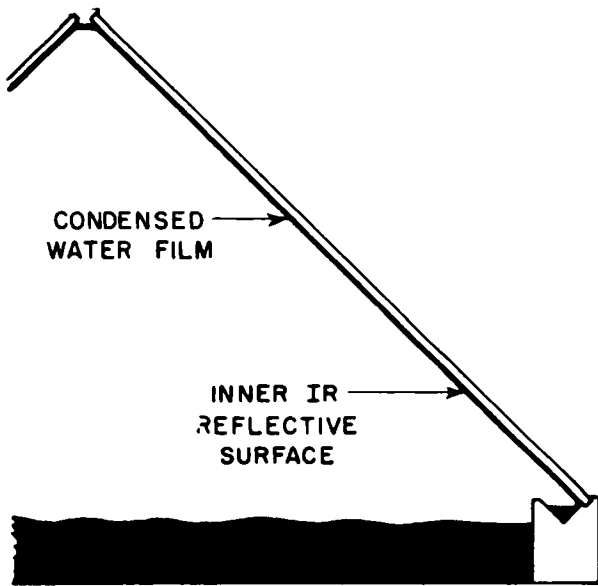WATER FILM

INNER IR
REFLECTIVE
SURFACE

ARRANGEMENT (D)

FIG. 8. SOLAR STILL CONFIGURATION WITH INFRARED REFLECTING
SURFACES APPLIED TO THE COVERING FILMS

improvement in this still configuration would be very small and almost
certainly negated by the additional cost of applying a low emissivity
coating.

Arrangement C is similar to Arrangement B in that a condensed
water layer is on the inside and a low-emissivity coating for IR is on
the outside of the cover. This design was intended to utilize some of
the heat taken up by the cover by circulating, very slowly, saline water
between two covering films and utilizing this heat by heat exchange and
storage to provide night-time distillation. A design with Glauber's
salt heat storage was made and analyzed rather thoroughly. With some
basic assumptions made, the OSW standard cost calculating procedures were
used to approximate the cost per 1000 gallons for a 6000 gallon per day still.
The cost per 1000 gallons calculated to be about $16, which is too high
to be practical even if the estimate is caused to be several times too
high by undue conservatism. This rather complex design, therefore, has
been ruled out of any further active consideration.

Arrangement D is the simplest design in terms of radiant energy
loss through the cover. In this design an external condensing system
is used, thereby avoiding a condensed water film on the cover. It is
noted that in the work of Professor Grune et al of Georgia Institute
of Technology high production rates have been obtained with experimental
stills using forced-convection and external condensers. The external
condenser system is the only type of which we are aware that permits
effective use of selectively infrared-reflecting coatings. This will be
the type system, therefore, being considered in connection with the
coatings described in the further sections of this report.

2. METALLIC COATINGS

Two general categories of selectively infrared-reflecting
surfaces were considered at the outset of the project. One category
was that of semi-transparent metal coatings. The other was that of inter-
ference-type reflection filters, both single and multiple film varieties.

The basis on which metallic films were cons. 'ered is that certain metals (e.g., gold) are known to have substantially higher reflectances in the infrared region than in the visible region. The principal problem is selectivity; that is, we wish to transmit almost all of the incident solar energy (λ_{max} about 0.51 μ) while reflecting a large part of the radiation re-emitted from the bath (λ_{max} about 9.25 μ). The second part alone is easy. A large number of vacuum-deposited metallic films will reflect greater than 95% of incident radiation at 9.25 μ wavelength. However, the reflection and absorption must be low for solar radiation. Various metals differ considerably in this respect.

Figure 9 illustrates the effect of wavelength of incident radiation on reflectance for vacuum deposited films of various metals. This was plotted from the data of G. Hass (Table 6K-4, reference (3) on freshly evaporated films of aluminum, silver, gold, copper and rhodium). We assume that these films are fairly thick, with rather low transmission; the effect of film thickness will be seen later. Some of the metals, such as silver, aluminum and rhodium, show little change in reflectivity from the 0.51 μ to 9.25 μ wavelength. These would not be useful therefore as selectively infrared-reflecting films. The copper and the gold, on the other hand, show a considerably lower reflectance at the solar λ_{max} than at 9.25 μ (though not as low as could be desired, however). Of these two, gold is the more interesting because of its chemical inertness (copper in thin films would be expected to oxidize or otherwise react chemically). Examination has been made of the reflectance properties of a number of other metals. The following were noted to have suitable chemical resistance and potentially useful reflectance characteristics: platinum, nickel, cobalt, tungsten, molybdenum, tin, tantalum and vanadium. Table 1 lists the reflectances of polished surfaces of these metals as a function of wavelength. (These data were gathered from compilations in the Handbook of Chemistry and Physics, 41st Edition, for the pertinent wavelength range.) The point of interest with these metals
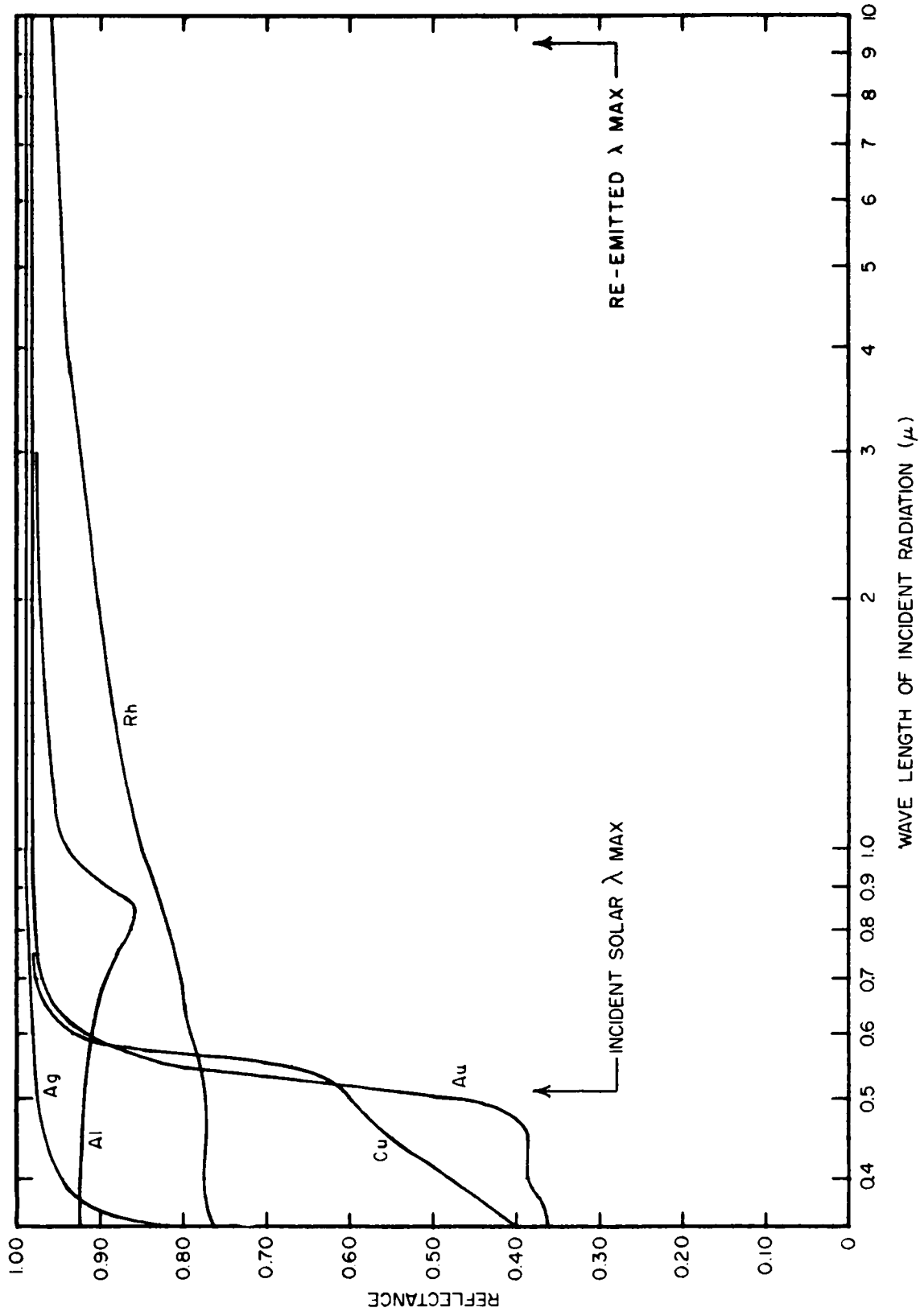
FIG. 9. REFLECTANCE VS. WAVE LENGTH FOR VACUUM-DEPOSITED METALLIC FILMS

Table 1

METAL REFLECTANCES AT VARIOUS WAVELENGTHS

Wavelength (microns)	Gold electrol.	Platinum electrol.	Nickel, electrol.	Tungsten	Cobalt	Molybdenum	Tin	Tantalum	Vanadium
0.42	0.293	0.518	0.566						
0.5	0.470	0.584	0.608	0.50		0.46		0.38	0.57
0.6	0.844	0.642	0.649	0.51		0.48		0.45	0.58
0.7	0.923	0.690	0.688	0.54					
0.8	0.949	0.703	0.696			0.52		0.64	0.60
1.0		0.729	0.720	0.60	0.67	0.58	0.54	0.78	0.61
2.0	0.968	0.806	0.835	0.87	0.72	0.82	0.61	0.90	0.69
3.0		0.888	0.887	0.92					
4.0	0.969	0.915	0.911	0.94	0.81	0.90	0.72	0.93	0.79
7.0				0.95	0.93	0.93	0.81	0.94	0.88
9.0	0.980	0.954	0.956		0.97	0.94			
10.0							0.84		

is that they all have, at short wavelengths, a longer region of reflectivity than does gold. This permits a sharper discernment between the solar wavelengths and the re-emitted wavelengths than with gold.

An analysis with the gold system, however, will serve to show the impracticality of the thin metal film approach for improving still efficiency. Figure 10 is an illustration of the transmittance-reflectance-absorption behavior of a thin gold film as a function of film thickness in the visible region. It is plotted from the data of Rouard, Male and Trompette presented in Figure 6.6 in reference (4). Notice that reflectance is very strongly affected by thickness, even more so than absorption over the 350 Angstrom range; note also, however, that absorption reaches almost its maximum in the first 50 Angstroms of thickness.

For the thin metal coating to be technically of any value the energy saved must be greater than or equal to the energy lost. If we assume 57% of the re-emitted radiation absorbed by the cover is lost (an approximate figure discussed at a later point), and assume that 100% of the solar radiation which passes the cover gets absorbed by the bath, and ignoring losses, the following expression relates energy saved and energy lost for a useful situation:

$$\overbrace{0.57(R_{c,i}-R_{u,i})(H_2O \text{ emissivity})(\text{radiant emittance})}^{\text{Energy Saved}} \geq \overbrace{(T_{u,s}-T_{c,s})(\text{solar irradiance})}^{\text{Energy Lost}}$$

where $R_{c,i}$ and $R_{u,i}$ are the reflectances for infrared radiation of the coated and uncoated cover materials respectively, and $T_{u,s}$ and $T_{c,s}$ the transmittance for solar wavelengths of the coated and uncoated cover materials respectively. The blackbody radiant emittance for a surface at 40°C is 546 watt/m^2 (see Figure 2). For water, which has an emissivity in this region of 0.96, the net radiant emittance is (0.96)(546) = 534 watt/m^2. Solar irradiance, which can vary over a wide range, was taken for this illustration as 1000 watt/m^2 of horizontal surface (within Abbot's figures for Washington, D.C. range of maximum intensities.)
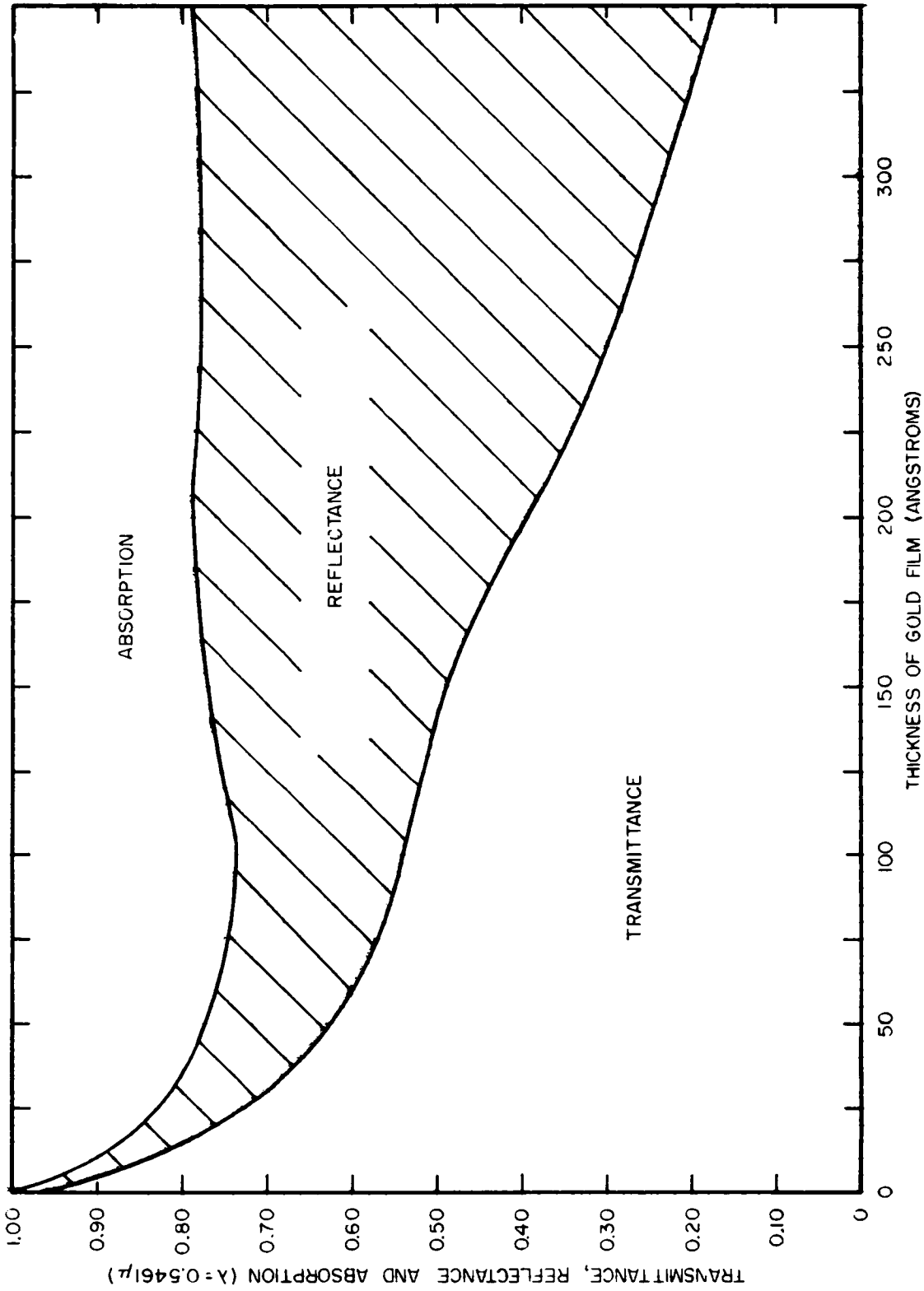
FIG. 10. TRANSMITTANCE, REFLECTANCE AND ABSORPTION VS. THICKNESS OF A VACUUM-DEPOSITED GOLD FILM, FOR LIGHT OF 0.5461 µ WAVE LENGTH

Transmittance of the solar energy for the uncoated cover, $T_{u,s}$, equals
1.0 minus the absorption and reflectance. The absorption is essentially
zero and the reflectance is about 8% (that is, 0.08); the transmittance
therefore is 0.92. Substituting these in the equation, we get:

$$0.57 \ (R_{c,i} - 0.05)(534) \geq (0.92 - T_{c,s}) \ 1000$$

or,

$$R_{c,i} - 0.05 \geq 3.29 \ (0.92 - T_{c,s})$$

Now to use this equation a transmittance figure, $T_{c,s}$, is
chosen; in this example we will choose 0.80, which is typical figure.
From Figure 10, which is plotted for a near-median solar wavelength (0.5461 μ)
the gold film thickness to give 80% transmittance is approximately 14
Angstroms and the reflectance for this wavelength is 0.074. From Figures
9 and 10 the reflectance of a thick gold film is about 10 times that much.
Assuming the proportion

$$\frac{R \ thin \ film, \ solar}{R \ thick \ film, \ solar} = \frac{R \ thin \ film, \ IR}{R \ thick \ film, \ IR}$$

to be approximately correct, and using the data in Figure 9 and Table 1,
a value of 0.098 for the reflectance, $R_{c,i}$, is obtained. Substituting
in the inequality expression, the final result is that

$$0.048 \not\geq 0.393$$

and thus that a 14 Angstrom gold film on the inner surface of the cover
will not work (by a very great margin!) and that a lower rather than a
higher basin temperature would result.

It is easy to see furthermore that other gold film thickness-
to provide 70% or 90% solar transmission, for example - will not work
either. Indeed, because the inequality is so far in the wrong direction
we see that improvements by a factor of two or three which might be obtained
by the use of thin films of other metals (having greater selectivity than

gold) in Table 1 are not sufficient to make this metal-film approach operative. For example, the highest ratio of IR-to-solar reflectance is about 2.5 with tantalum. This is not nearly enough to offset the absorption losses (over and above the reflection losses) in the solar region.

The conclusion then is that the thin metal film approach for preventing radiant heat loss through the still cover is not feasible in any case.

3. INTERFERENCE-TYPE SYSTEMS

Interference reflection systems are fundamentally different from the thin metal systems in that the interference systems are essentially non-absorbing and are dependent on thickness for wavelength of maximum reflectance. The interference systems were considered in two categories: the single layer systems, and the multiple layer systems with alternating layers of high and low refractive indexes.

The first study was with the single layer systems as they are simpler to analyze and are lower in applied cost than the multiple layer systems. For single layer films of refractive index higher than the substrate, maximums in reflectance are obtained for odd integral multiples of $\lambda/4$, where λ is the wavelength of incident radiation. For the thinnest film of maximum reflection the relationship is

$$d_1 = (2m + 1) \frac{\lambda}{4 \, n_1}$$

where d_1 is the film thickness and n_1 is the index of refraction of the coating at λ. For $\lambda = 9.25 \, \mu$, n_1 for TiO_2 is (by an extrapolation) approximately 2.4, and d_1 is 9640 Angstroms. This is a higher film thickness than that usually encountered in thin film practice.

The following equation is used to determine the maximum reflectance, (R) max, for a single-layer $\lambda/4$ "tuned" system (assuming no absorption):

$$R\ (max)\ =\ \frac{(n_1^{\ 2}\ -\ n_o\ n_2)^2}{(n_1^{\ 2}\ +\ n_o\ n_2)}$$

where n_o is the index of refraction of the exterior phase (which in this case is air = 1.00), n_1 is the index of refraction of the coating (in this case, TiO_2 at 2.4) and n^2 is the index of refraction of the substrate (in this case, Tedlar estimated at 1.4 for λ = 9.25 μ). Substituting, we get R(max) = 0.371. This is not the reflectance over the entire re-emitted spectrum, however; the reflectance decreases in both directions from this 37.1% maximum. The integrated reflectance of the re-emitted energy (based on considerations further presented with the 5-layer system) would only be about 20%. This works out to a power saving of 47 watts/m^2, which is a little less than 5% of the incident solar power. As a 5% output improvement can be obtained by merely increasing the still area by 5% (at a capital cost increase of that order) we can get some idea of the maximum useful cost of the coating from the still cost per unit area; for example, in a $1.00 per square foot still the coating cost should not exceed $0.05. Using what appears to be the simplest material and coating technique, that of chemically depositing TiO_2 (its choice to be discussed later) it appears that about 20 uniform coats of approximately 500 Angstroms each would be needed. That this could be done for $0.05 or 0.10 per square foot is doubtful indeed. Thus our conclusion is that while the single film interference coating system may be technically feasible, it is economically impractical (costing more than it saves.)

While the maximum reflectance of the single layer interference systems is limited (to 37.1% with TiO_2, which is the highest refractive index material with solar transparency of which we are aware), multiple layer interference filters can attain reflectances of greater than 95% for a given wavelength. An odd number of films having alternately high

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and low refractive indexes and having thicknesses if $\lambda/4$ (path difference of $\lambda/2$) produce maximum reflection at wavelength λ_0. Vašiček (p.235, reference (5)) tabulated the reflectance for various numbers of $\lambda/4$ layers in which $n_1 = 2.40$ (high index material) and $n_2 = 1.36$ (low index material.)

Table 2 lists some of these figures.

Table 2: Reflectance for Multiple-Film Interference Systems

Number of Films	Reflectance %	Effective Index of Refraction (Equivalent for Single film of same Reflectance)
1	33.97	2.400
3	71.23	4.235
5	89.70	7.474
7	96.57	13.19
9	98.88	23.28

It can be seen that maximum reflectance increases to very appreciable levels with an increasing number of films. As the complexity in coating increases steadily with increasing number of coats our study was directed primarily at the 3 and 5 coat systems.

From the data in Figure 64 of Vašiček (5), reflectivity vs. wavelength was plotted for a maximum reflectivity at the $9.25 \lambda_{max}$. This plot is given in Figure 11 with both phase difference, x, and wavelength shown on the horizontal axis. The plot is for a 5 layer system with $n_1 = 2.40$, $n_2 = 1.36$, and $n_0 = 1.52$ (the substrate).

Figure 12 is a dual plot of spectral emittance of a blackbody at 40°C vs. wavelength (as in Figure 3) and spectral reflectance with the above-mentioned 5 layer system. The latter curve was obtained by multiplying spectral emittance values at given wavelengths by the corresponding reflectivity values from Figure 11 to obtain the spectral reflectance values. The area under each curve in Figure 12 is a direct measure of the power per unit area $(watts/m^2)$.
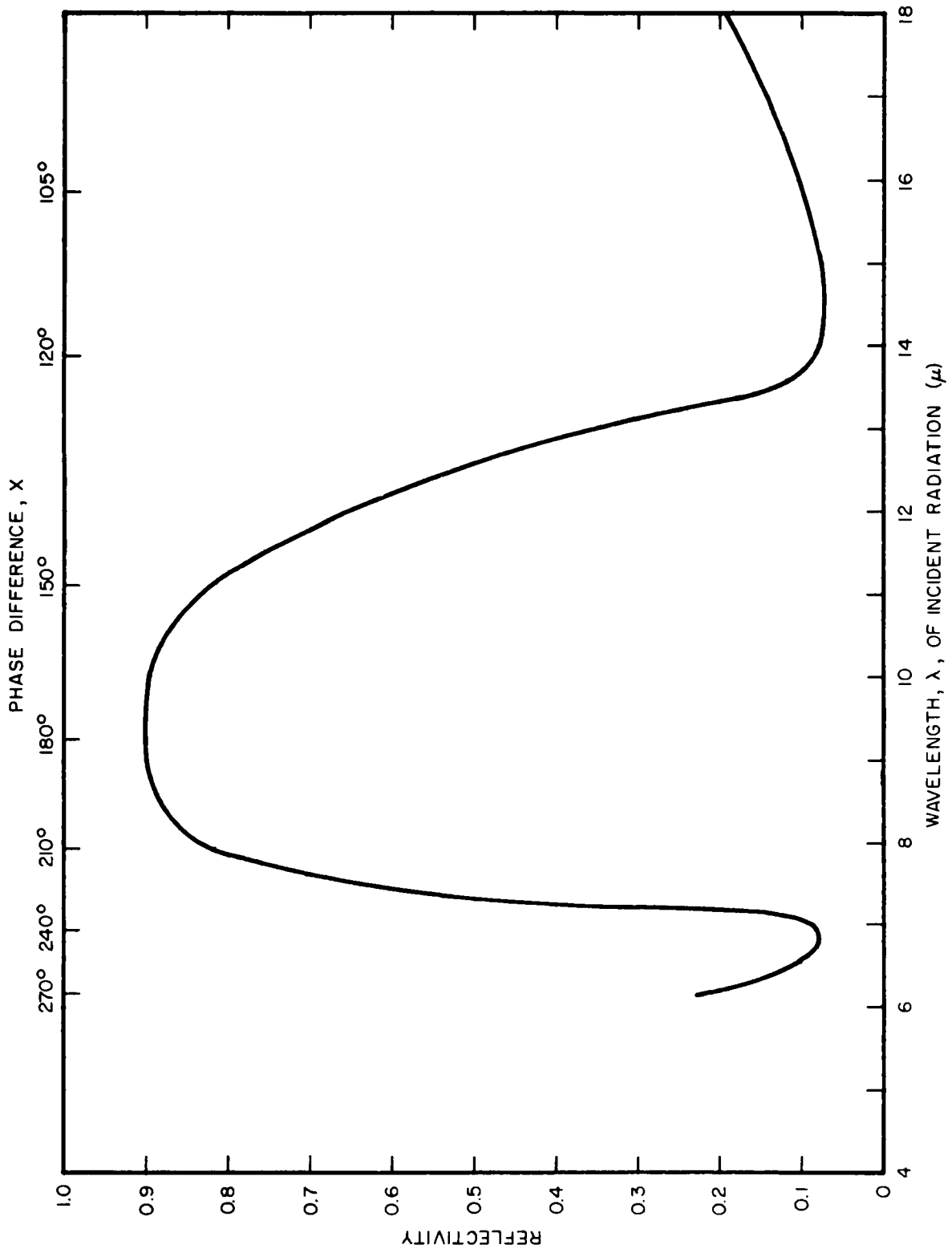
FIG. II REFLECTIVITY VERSUS WAVELENGTH FOR A 5-LAYER INTERFERENCE REFLECTING FILM
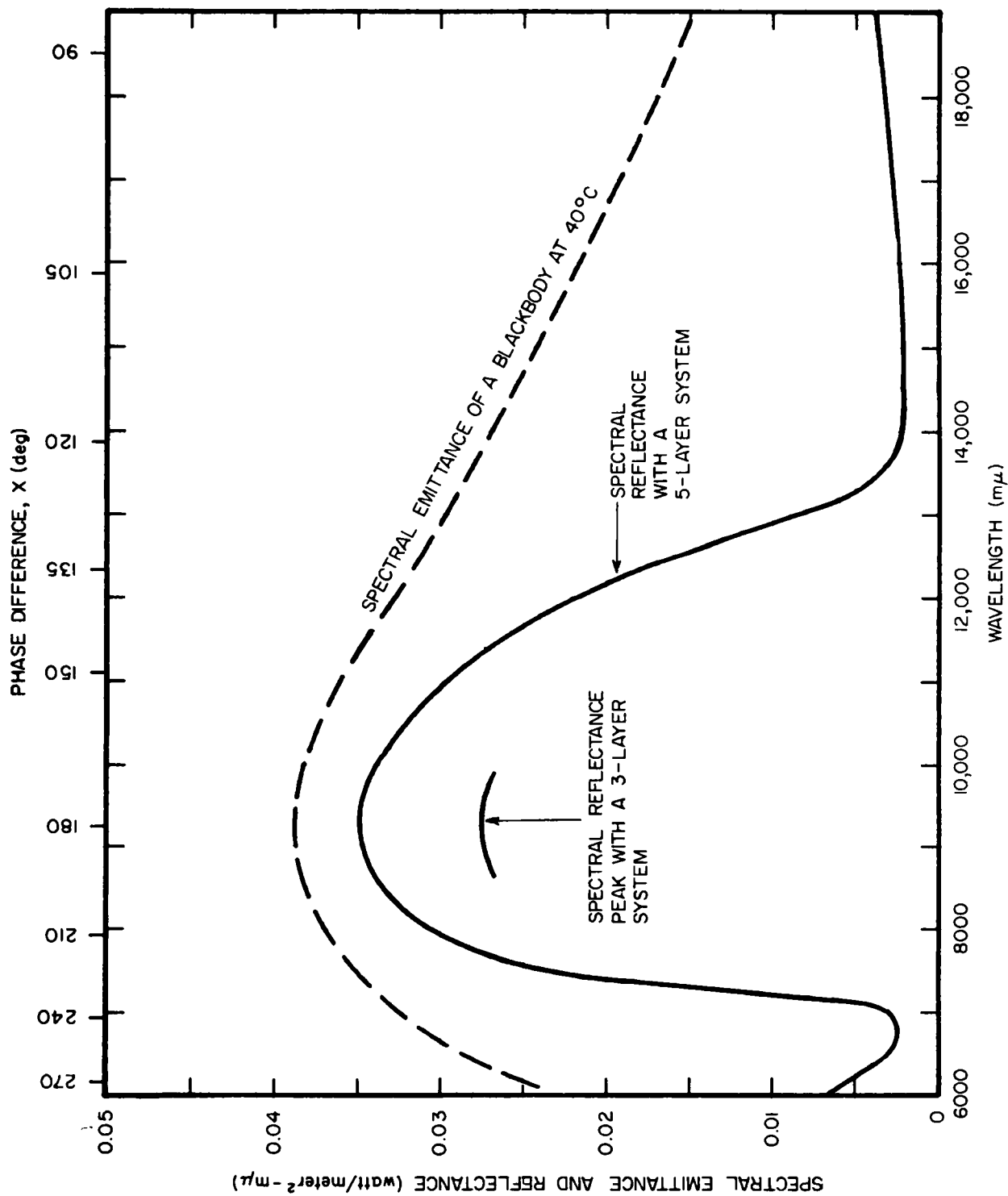
FIG. 12. SPECTRAL EMITTANCE AND REFLECTANCE VS. WAVELENGTH FOR A 40°C BLACKBODY EMITTER AND MULTIPLE LAYER REFLECTING SYSTEMS

This power was measured in each case directly from Figure 12. Under the overall emittance curve from 6000 to 19000 mμ the power is 374.2 watts/m^2. Under the corresponding reflectance curve the power is 181.8 watts/m^2. Thus for the 6000 to 19000 mμ range the hypothetical 5 layer system will reflect 181.8/374.2 or 48.6% of the emitted radiant power (or energy for a given time period.) Now the total radiant emittance for a blackbody at 40°C is 545.8 watt/m^2. Therefore 545.8 - 374.2 or 171.6 watts/m^2 is emitted outside the 6000-19000 range. Assuming a mean of 18% reflection over the rest of the range, we have (.18)(171.6) or 30.9 watts/m^2 reflected. Thus the overall emittance is 545.8 watts/m^2, the overall reflectance 212.7 watts/m^2 and the overall efficiency of reflecting the radiant energy back to the basin is 39.0%. (If we assume more correctly that the water has an emissivity of 0.96, the 39% figure still holds though the absolute value of the emittances and reflectances would be smaller by that factor.)

The reduction in radiant energy loss from the bath using the hypothetical 5-layer system deposited on a cover which for its thickness would absorb most of the IR is not 39%, however. For a glass cover all the re-emitted radiation not reflected would be absorbed; for a Tedlar (vinyl fluoride polymer) cover, on which we experimentally measured IR absorption from 2-15 μ with the Perkin-Elmer Model 21 Infrared Spectrophotometer, most but not all (greater than 85%) is absorbed if not reflected. For the non-condensing cover the absorbed energy is removed by radiation and conduction-convection processes. If the cover is of uniform temperature across its thickness the radiant emittance from each side is equal. As a very rough estimate let us assume that 4% of the radiant energy incident to the uncoated cover if reflected back to the bath, and 96% absorbed; of this 96 parts let us assume that 10 parts are lost by conduction-convection and 43 parts radiated inward and 43 outward. (There is no net loss by conduction-convection to the inside, but rather again, as the enclosed still air is generally warmer than the cover.)

Thus, ordinarily 4 + 43 or 47% of the emitted energy is returned to the bath. In our case 39% is initially reflected back to the bath. If we assume the energy absorbed by the cover to be distributed as above 27 + 39 or 66% would be returned to the bath. These are crude estimates not taking into consideration such factors as absorption of the long-wave irradiation by the humid air or change is emissivity of the cover by the reflective coating.

Now taking again a value for incident solar power of 1000 watts/m^2 the efficiency improvement resulting from the reflecting coating can be estimated. The emittance of the bath is 524 watts/m^2. The ordinary cover would return approximately (.47)(524) or 246 watts/m^2. The 5-layer reflecting cover would return (.66)(524) or 346 watts/m^2. This is a 100 watt/m^2 improvement cr 10% of the total maximum solar power incident on the still. (The opposing factors of differences in solar reflectance loss and differences in radiant loss proportions under lower solar energy and night-time conditions have been neglected in this calculation.) Thus if a basic still cost of $1.00 per square foot of evaporating basin is being considered (horizontal roof) the total cost of treating the cover film may not exceed $0.10 per square foot. Likewise for a $2.00 per square foot still the maximum figure is roughly $0.20 and for a $0.50 per square foot still the figure is roughly $0.05 per square foot. The economic problem arises as to whether a multiple-film interference reflection filter can be made for 5 or 20 cents per square foot. Commercially available multiple-film interference filters for visible and near infrared (e.g., 1-2 μ) regions cost in the order of 100 and 1000 times this, though admittedly these prices are for small-area (e.g., 4 square inch) optical filters, and substantial economies should result in large-scale application. This, however, could be offset by the fact that multiple depositions would be required for each layer in our system because of the great thicknesses involved. Materials and method of application will be discussed subsequently.

A 3-layer system would be somewhat less expensive to prepare but also be lower in radiant reflectance. The level of maximum reflectance is shown on Figure 12. The 3-layer system would be intermediate in economics between the 1-layer and 5-layer systems discussed above.

The technical feasibility of making a multi-layer interference reflection system with maximum reflectance at about 9.25 μ was at one point in doubt. What are required are two materials: one with a low index of refraction (1.4 or less) and one with a high index of refraction (2.0 or more) in the infrared region. In addition each material must have the following four properties: (1) be essentially insoluble in water; (2) have low absorption in the solar wavelength region; (3) have low absorption in the long-wave infrared region; (4) be stable under extended solar irradiation.

The first requirement, which is important even in external-condenser stills where condensation inside the cover may occur at night, eliminates the many alkali-metal halides which are common infrared optical materials.

The second requirement, for solar transparency, causes rejection to a large degree of such infrared optical materials as germanium, selenium, tellurium and arsenic trisulfide. The best of these, selenium, might also be rejected on the basis that it behaves much like arsenic in toxic characteristics.

The third requirement is for low absorption in the 9 μ IR region; this eliminates the great mass of water-insoluble and solar-transparent materials, such as glass, metal oxides, metal silicates, etc. Films with high absorption do not permit the operation of the interference reflection principle; with moderate absorption the maxima and minima in the reflectance curves are displaced in the direction of those with thinner transparent films.

The fourth required property, stability to solar radiation, eliminates silver chloride, which otherwise would be of value as a high-index material.

These requirements rule out completely all but a very few materials for use in the interference system. For the low-index material, calcium fluoride appears to satisfy fairly well all the requirements (n = 1.33 at 9 microns; solubility = 0.0017 g per 100 ml of water; transmission in thick sections to 10 microns, further in thin sections; stable under solar irradiation; transparent to solar radiation.) Magnesium fluoride would also be of some interest, although it is somewhat more soluble in water (0.007 g per 100 ml of water.)

To find a suitable high-index material has taken more time and required an experimental program involving preparing thin films. After substantial literature research the one material which appeared best to fulfill the above four properties was strontium titanate. The absorption coefficient, α, at 9 μ is 65 cm^{-1}, and at 10 μ is 100 cm^{-1}. For a 1.16 μ thickness film the absorption at 9 μ is 0.75% and at 10 μ is 1.15%. These represent satisfactory levels for interference film purposes. An experimental program was undertaken to attempt to prepare vacuum deposited films of strontium titanate from an ultrapure powdered sample. As this is a refractory material, ordinary resistance-heating thermal evaporation would not be satisfactory. An electron beam evaporation set-up was constructed, and an attempt made to deposit strontium titanate on a glass substrate. Only thin discolored films were obtained; probably two difficulties were present: (1) the temperatures were too low with our apparatus; (2) some degradation (reduction) of the titanate was occurring. Because of the large amount of effort expected for continuing with this approach, study was made of other materials which fulfilled all qualifications except for being absorbers of 9 μ IR in thick sections (which are what the literature usually reports on.)
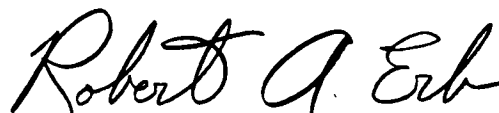
The most interesting material which appeared was titanium dioxide which has fairly good near infrared transmission and which is particularly interesting as it can easily be chemically deposited (as done in the earlier program for OSW on the preparation of permanent hydrophilic surfaces on solar still condensing surfaces.) No report was found in the literature on the absorption of thin films for the 8-15 μ wavelength region. It was thus decided to run transmission curves on the infrared spectrophotometer. The substrate on which the TiO_2 was deposited was Kodak Irtran-2 Infrared Optical Material, which is a water-insoluble material having good transmittance in the 2-14 μ wavelength region.

Two equal-thickness flats of Irtran-2 were used, with one being placed in the reference beam. The other was coated with TiO_2 from a 6% by weight solution of tetraisopropyl titanate in hexane by uniform-withdrawal dipping. The coating was made on one side only (the side facing the source light) by masking. This concentration of solution, from earlier interferometric measurements, is known to deposit approximately 500 Angstroms thickness of TiO_2 per dip coat at 8 inches per minute withdrawal speed. To obtain a 10,000 Angstrom coat, many thin coats must be laid down. Thick single coats flake easily. For our study 10, 20 and 40 deposited layers were made and their IR transmission measured. For a 40 layer film of about 20,000 Angstroms (equivalent to the total TiO_2 thickness in a 3-layer interference system) the transmittance at 9.25 μ was approximately 88% and not much less than this at any point. As some of the reduction in transmittance is from reflection losses, the absorption level appears to be satisfactory for use of the TiO_2 in multiple-film interference filters.

Thus, we feel, the technical feasibility of producing multiple-film interference reflection coatings on a substrate, wherein the efficiency of use of the incident solar energy will be enhanced, has been demonstrated. At the same time, however, the requirement for very thick "thin films,"
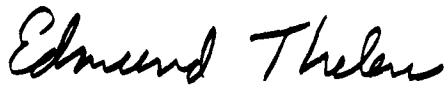
with multiple depositions per film and careful thickness control through-
out, militate so severely against economical production that it is
doubtful that th-- :o.: ;:. ..!. ..ea can get within a factor of ten even
of a useful figure (such as $0.20 per square foot) even with very large
scale production.

The overall conclusions from this project are that: (1) the thin
metal film approach is technically infeasible; that is, it will not
provide a physical enhancement of solar energy utilization; (2) the
interference film approach, both with single and multiple-film systems
is technically feasible, but economically infeasible, because of the
many-times greater cost of applying the coatings than the maximum allowed
for the benefits received.

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