

Selective Coatings for Extraterrestrial Solar Energy Conversion; A Fundamental Analysis

Robert M. Van Vliet
Materials Central
Wright Air Development Division

I. SUMMARY

This report discusses the role of solar energy in the overall problem of secondary power generation for space vehicles. The principal technology needed for the successful use of solar power is that of achieving high solar energy collection efficiency. The author has analyzed the optical variables entering into coatings for the collection of solar energy and expressed these variables in graphical form suitable for use in future analysis of this type. The result of this analysis leads to a graph of collection efficiency vs temperature which completely characterizes a coating for solar power generation. This study points up the need for coatings with high solar energy absorption, α , as well as high α to ϵ ratios. The fundamental principals of energy absorption and reflection are discussed with reference to metallic and dielectric materials. The application of these principals to selective coatings is discussed and illustrated.

II. INTRODUCTION

The short lived satellites and space probes of today receive their "secondary" power (to drive their instruments and transmitters) from batteries. When the satellite is designed to last for longer periods, it is more profitable to incorporate a power system to recharge the batteries and thus reduce the weight of batteries necessary to power the accessory equipment. There are two potential sources of this secondary power, i.e., nuclear fission and solar energy, respectively.

Nuclear power is essentially similar to a long lived, very efficient battery in that it is a concentrated source of energy but it does run down. Both radioactive isotopes and fissionable materials compete for use as secondary power sources and may find application to some future space vehicles. However, they suffer from high cost and the nuclear reactor, which uses fissionable material, poses many problems of developing compatible electrical and mechanical equipment. If these problems are overcome, the nuclear reactor will be considered for space systems where very high levels of power are required.

The sun, as an alternate source of power, appears very attractive. It presents relatively minor materials problems and is a constant source of energy varying only about 3 percent throughout the year for Earth satellites. Therefore, it remains only to develop efficient solar energy collection techniques to tap this inexhaustible energy source.

Solar energy may be converted to electrical power by direct and indirect methods. The direct method, exemplified in the photovoltaic cell is quite effective as a very small power source. However, only about one-third of the solar radiation (in a narrow wavelength band) is usable for direct conversion to electricity in present day photoelectric cells. The rest of the energy must be reflected for best output of the cell. In the indirect method the sun is used merely as a source of heat. In this case, reflected solar energy represents a loss of power so maximum absorption of solar energy is desirable.

Since high absorption of solar energy is easily obtained, the reradiation of this energy becomes the chief loss of power. Unfortunately, with most coating materials, high solar energy absorption corresponds to high emittance*. There are several approaches to overcoming this and achieving high solar energy absorption with low emittance. The most promising of these are being explored by Materials Central, Wright Air Development Division. The "interference" coating, which is one of the most refined approaches to this problem, has been used as an example in this paper and is described in more detail below.

In order to achieve high thermodynamic efficiency in a power system, a high temperature heat source is necessary. To obtain this high temperature, you can use a "flat plate" collector with a selective coating or a "green house", or you can employ a parabolic mirror to concentrate the energy. In either case, the relationship between the heat absorbed to that reradiated to space is the same. Therefore, a general approach for balancing the collection efficiency of the selected power system is developed below. The flat plate collector is used as the basis of the optical study because it is simpler and can be reduced to practice in the near future. Thermoelectric power systems appear most promising for the flat plate collectors while closed cycle gas turbines and thermionic systems look more desirable with parabolic light concentrators.

III. SOLAR ENERGY AVAILABILITY

It is the intensity of solar energy that makes it useable as a power source. Since the intensity of light varies inversely with the square of the distance from the source, solar energy becomes a little sparse around the outer planets. This is shown in Table I. It should be noted that the collector area becomes quite large at planets more distant than Mars even when assuming a constant energy conversion efficiency. Since the energy conversion efficiency also drops with reduced heat intensity, it can be seen that Mars is about the limit for the profitable use of solar energy.

* Emittance is the power of a coating to radiate heat as compared to a theoretical black body at the same temperature.

TABLE I

SOLAR ENERGY AVAILABLE IN THE SOLAR SYSTEM

Distance Equal to:	Solar Energy Watts/cm ²	Collector Area per Kilowatt*	Temperature of a black Sphere	
Mercury	0.92	1.1 M ²	175°C	341°F
Venus	0.26	3.8	55	131
Earth	0.14	7.1	7	44
Mars	0.059	17	-48	-54
Jupiter	0.0051	200	-152	-242
Saturn	0.0011	900	-191	-312
Uranus	0.00037	4000	-210	-346
Neptune	0.00015	6700	-223	-369
Pluto	0.000092	11000	-229	-380

* Assuming 10% overall conversion into power

IV. TEMPERATURE CONTROL WITH COATINGS

In a body in space, all energy must be received and emitted by electromagnetic radiation or light (ultraviolet, visible and infrared). Since this energy is received and re-radiated by the exterior surface, the optical properties of the surface will control the heat balance. Figure 1 shows how this is possible. The energy emitted by the sun is at short wavelengths, with 94% at wavelengths shorter than 2 microns. On the other hand, the heat radiated by bodies even at 1200°K have only 14% of their radiated energy shorter than 2 microns. Thus, a coating, such as white paint, which is reflective to solar energy but is absorbtive (or emissive) at wavelengths longer than 3 microns will be cool. In contrast, a coating that has high absorption to solar energy and is reflective (or non-emissive) in the infrared, such as cupric oxide on copper will be heated to high temperature.

A. The Heat Balance

The energy entering a body in space is dependent on three factors, as follows: the solar flux, S, the absorption of this energy, α , and the area exposed to the solar flux A_s. Thus, the heat input, q_s, of a body in space is:

$$q_s = S \alpha A_s \quad (1)$$

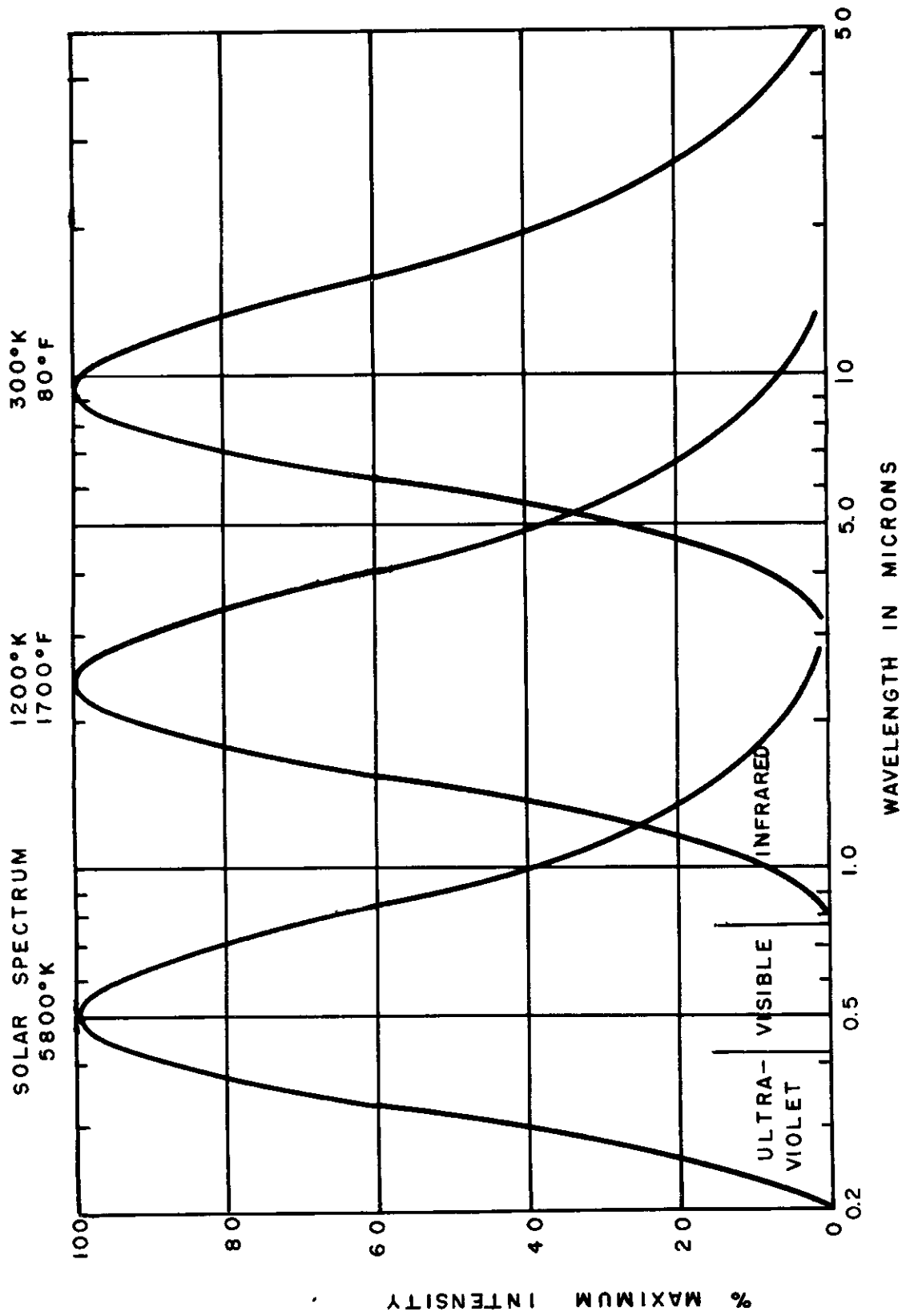


Figure 1 The Relative Distribution of Energy Radiated From Sources at Different Temperatures

Contrails

Energy may also be added as internal energy of a space vehicle due to friction, electrical resistance, etc. However, in this study, we are more interested in the energy removed from the system as a source of power, q_p . Of course, the remaining energy, q_e , is re-radiated to space. Thus:

$$\begin{aligned} q_s &= q_p + q_e \\ \text{or} \quad q_p &= q_s - q_e \end{aligned} \quad (2)$$

The emitted energy is controlled by the area for radiation, A_e , the temperature, T , and emittance, ϵ , as follows:

$$q_e = \sigma \epsilon T^4 A_e \quad (3)$$

where σ = Stefan-Boltzmann constant

From equations 1, 2, and 3

$$q_p = S \alpha A_s - \sigma \epsilon T^4 A_e \quad (4)$$

For a flat plate collector $A_s = A_e$ if you neglect the energy radiated from the back side of the collector plate. Since S and σ are constants the equation can be expressed as:

$$q_p = k_1 \alpha - k_2 \epsilon T^4 \quad (5)$$

where k_1 and k_2 are constants

Where $q_p = 0$ (no power load) then the α/ϵ ratio controls the temperature, i.e.

$$T^4 \sim \alpha/\epsilon \quad (6)$$

The temperatures resulting from this zero power loading are shown in Figure 2. These curves represent the maximum temperature obtainable with a flat plate collector. It will be noted that these temperatures are much higher than those listed in Table I because we are considering only a flat plate here (rather than a sphere) where the area for heat radiation is the same as that for heat absorption. As heat is removed from the flat plate collector to produce power, the temperature is reduced. Since no heat is removed from the collector plates graphed in Figure 2, the collection efficiency* is zero. Thus, higher collection efficiency must be achieved at lower temperature where thermodynamic efficiency is sacrificed.

Figure 3 is a plot of the temperatures of a flat plate located one astronomical unit** from the sun. The temperatures are expressed in terms

* Collection efficiency is the fraction of the total solar energy incident on the body that is available for power generation.

**An astronomical unit is 93 million miles, i.e. the distance from the Earth to the sun.

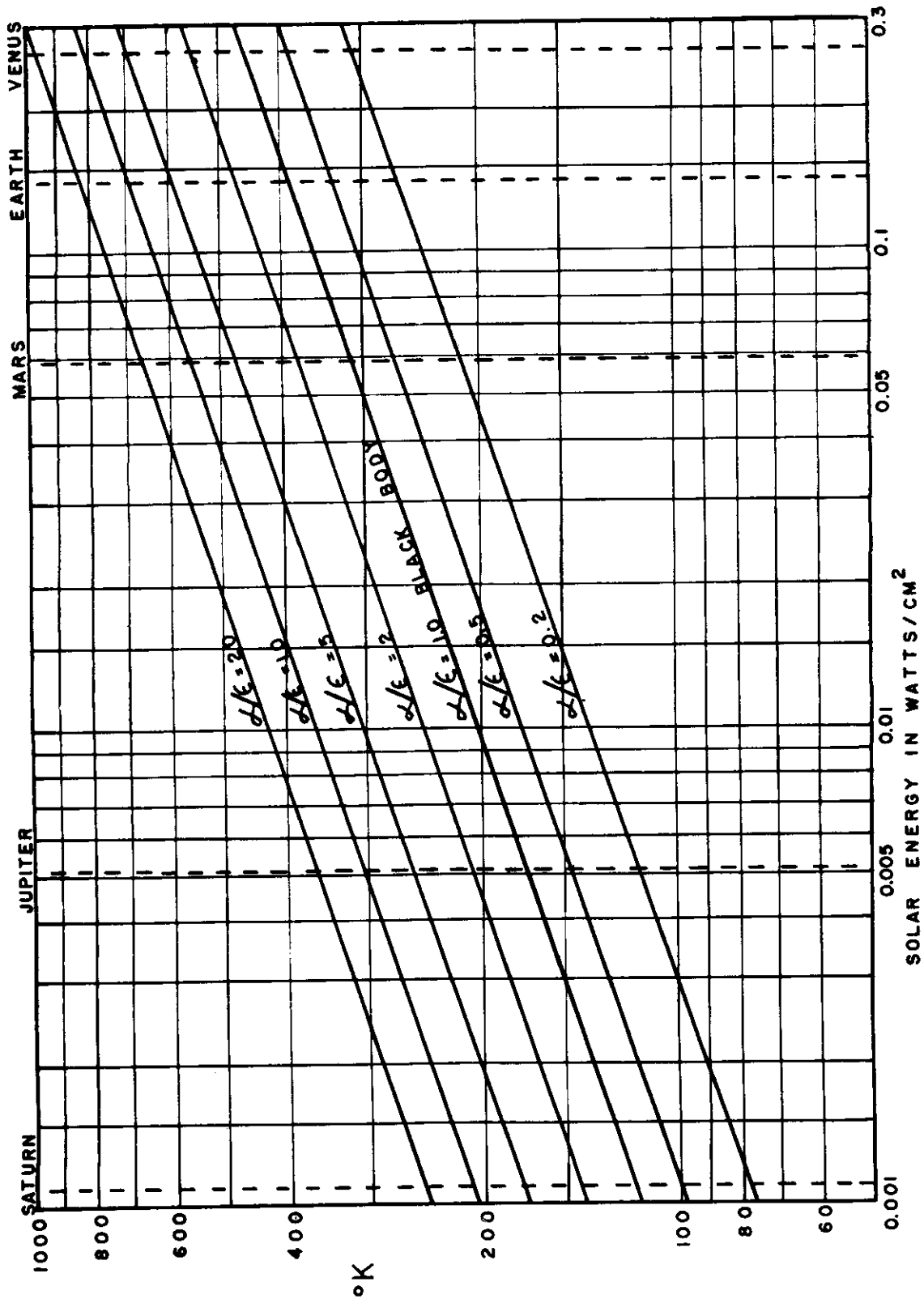


Figure 2 The Solar Energy Available in the Solar System and the Temperatures Produced on "Single Face" Flat Plate Collectors (Neglecting the Back Side Heat Losses).

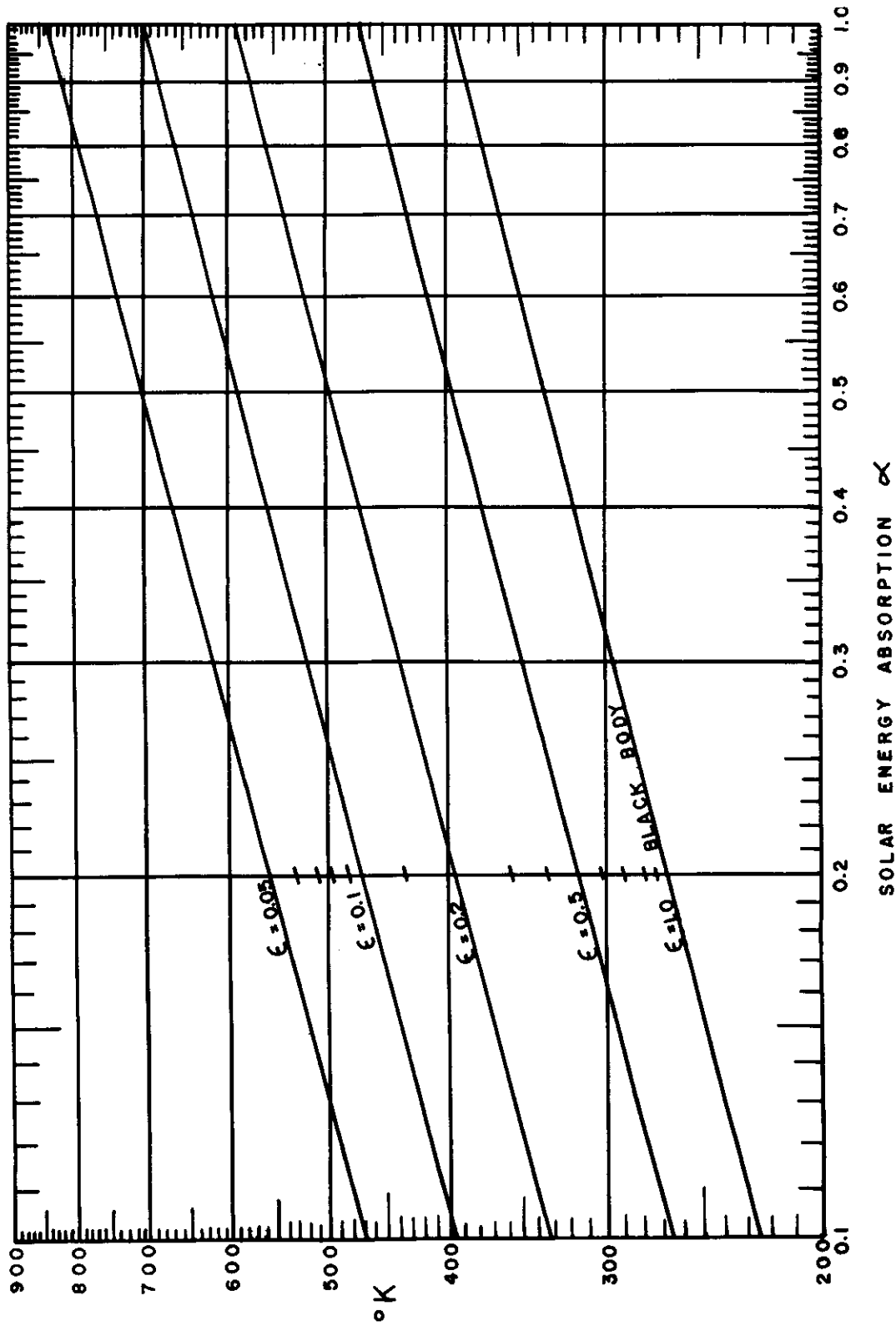


Figure 3 The Relationship Between Emittance, Temperature and the Rate of Heat Radiation Plotted Against the Available Solar Energy

of the optical properties of the coating, i.e. its absorption, α , and emittance, ϵ , respectively. Since this plot is based on the fraction of solar energy absorbed and emitted at any given temperature, it will give the collection efficiency by the difference. For instance, if $\alpha = 0.9$ and $\epsilon = 0.05$, the collection efficiency will be 40% at 700°K and will be 80% at 470°K.

Figure 4 has been derived from Figure 3 by first plotting the collection efficiency against the temperature and the α to ϵ ratio assuming 100% solar energy absorption*. The collection efficiency can then be corrected for the actual solar energy absorption in the correction chart. For example, if $T = 700^\circ\text{K}$ and $\alpha/\epsilon = 20$, the collection efficiency is 50% for $\alpha = 1.0$ or 10% for $\alpha = 0.6$. Therefore, it can be seen that high collection efficiency at high temperature is achieved only by high α and high α/ϵ .

B. Application to a Practical Coating System

The so called dark mirror which absorbs light by optical interference is one of the approaches to obtaining selective energy absorption. This coating is described in more detail in the next section. An example of an Aluminum-silicon monoxide dark mirror is shown in Figure 5(1). The transition from an absorber to a reflector between 1.5 and 3 microns is almost ideal for a flat plate collector.

Figures 6 and 7 show graphically the relative absorption to solar energy and energy from a 600°K radiator, respectively. The absorption of energy from the 600°K source should approximate the emittance of the coating at 600°K, assuming that the absorption is independent of temperature (a fair assumption for most materials).

The absorption process is discussed in more detail in section V below. It is worthwhile noting here that metal absorption of infrared light varies directly as the square root of its resistivity and inversely with wavelength. Therefore, spectral emittance would increase with temperature in the same relationship to resistivity. However, total emittance would be further increased by the shift in wavelengths (see figure 1) in accordance with Wein's displacement law.

Figure 8 shows the application of the coating collection efficiency calculator to this dark mirror coating. This coating has a computed α/ϵ of 18.2 with an α of 0.91 up to 700°K. Based on published emittance data for aluminum, this curve should slope more to the right for higher temperatures which would reduce the high temperature collection efficiency somewhat.

* Without this assumption a whole series of lines would result for each absorption value.

(1) Hass, G., Schroeder, H. H. and Turner, A. F. "Mirror Coatings of Low Visible and High Infrared Reflectance" J. Opt. Soc. Am 46, 31 (1956).

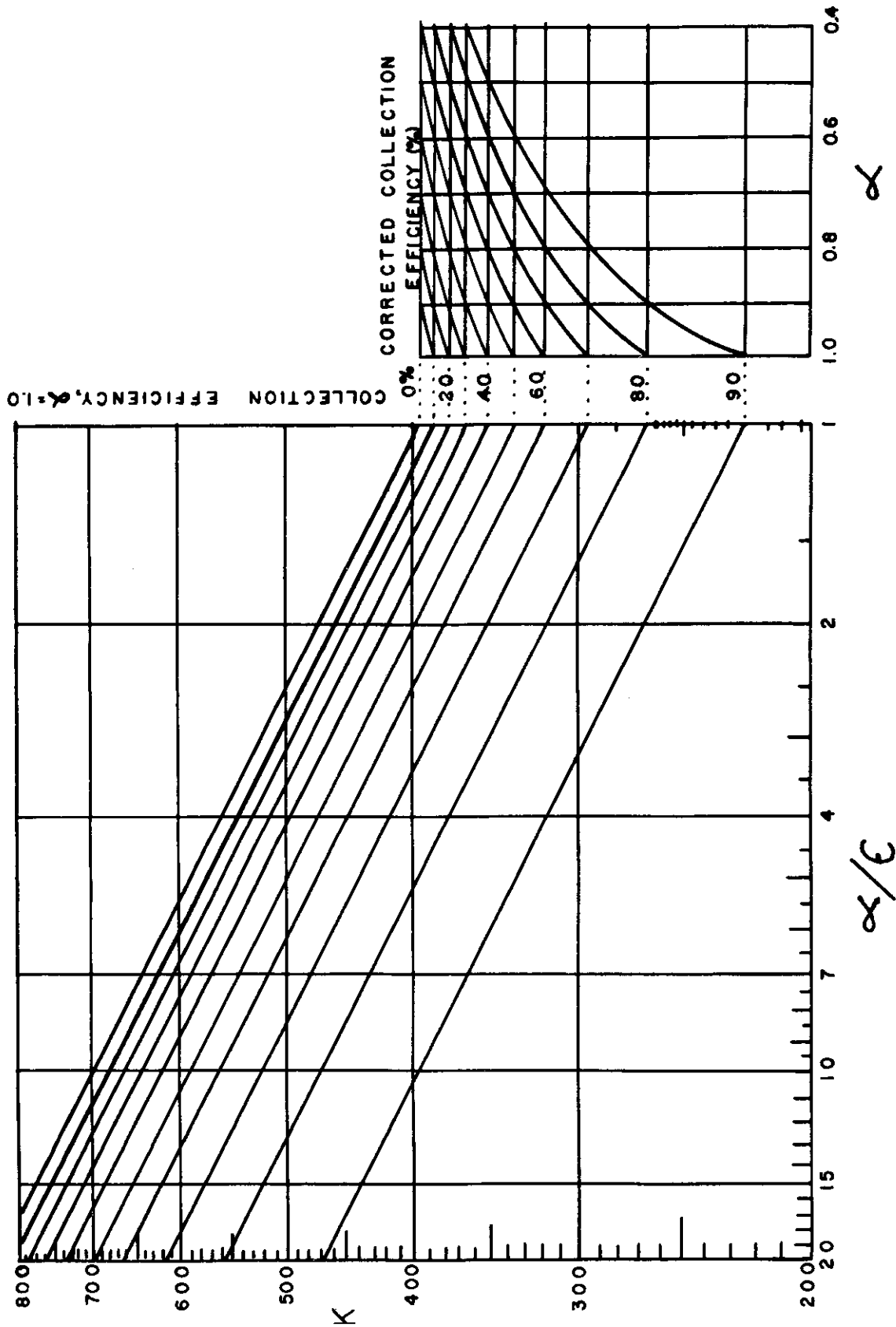


Figure 4 The Coating Collection Efficiency Calculator

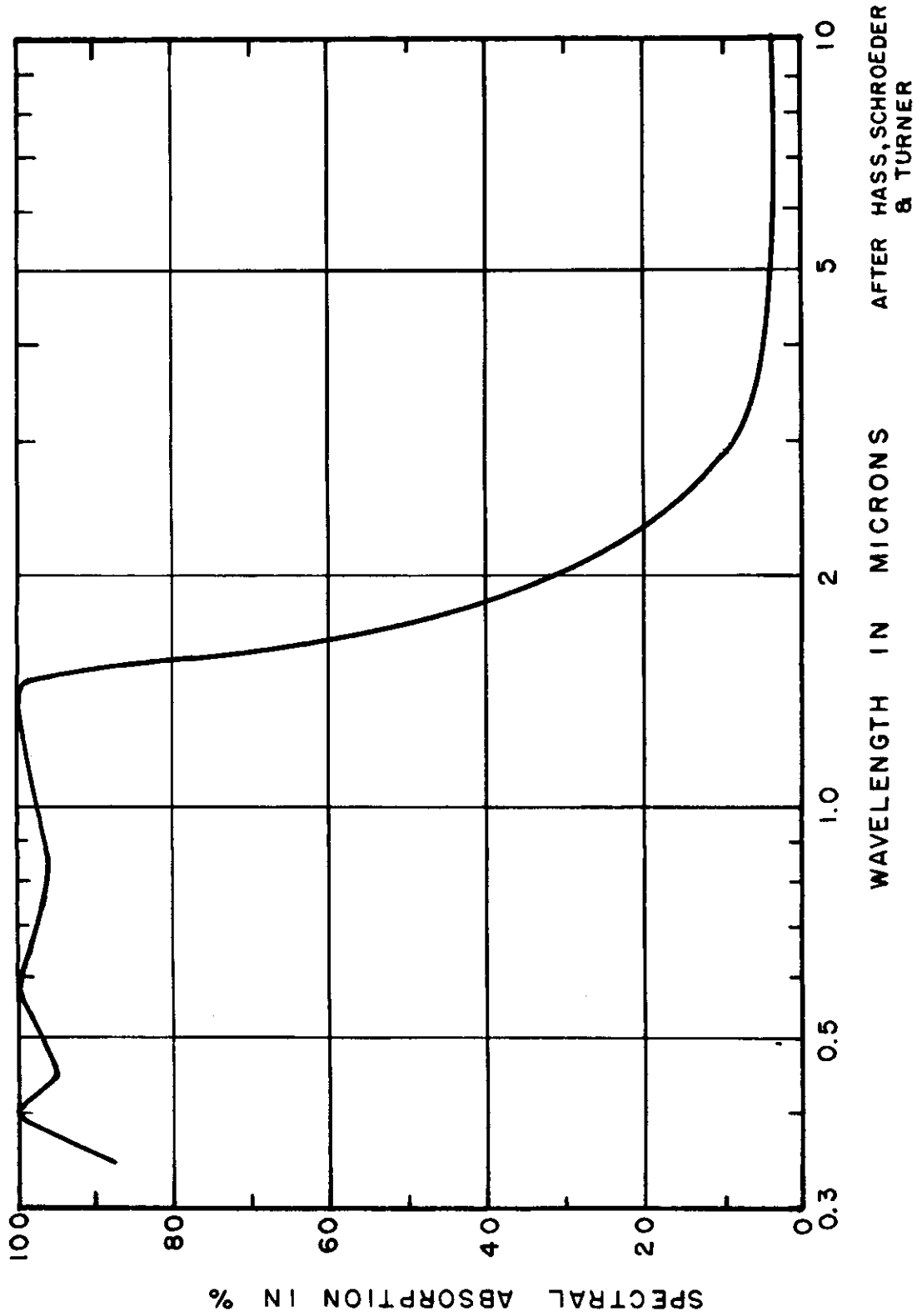


Figure 5 The Spectral Absorption of an Al-SiO-Al-SiO Dark Mirror or Interference Coating

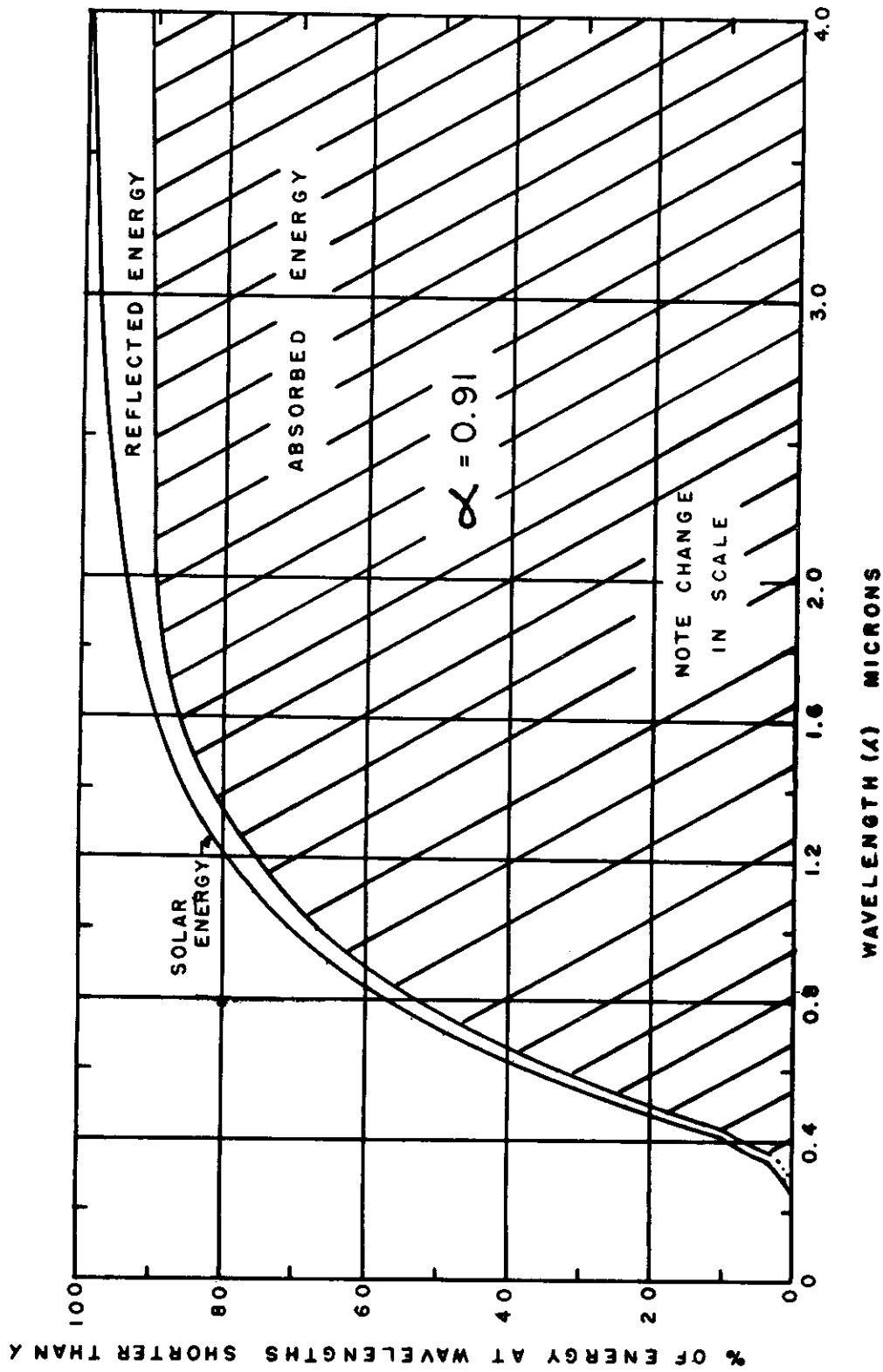


Figure 6 The Solar Energy Absorption of the Dark Mirror Coating

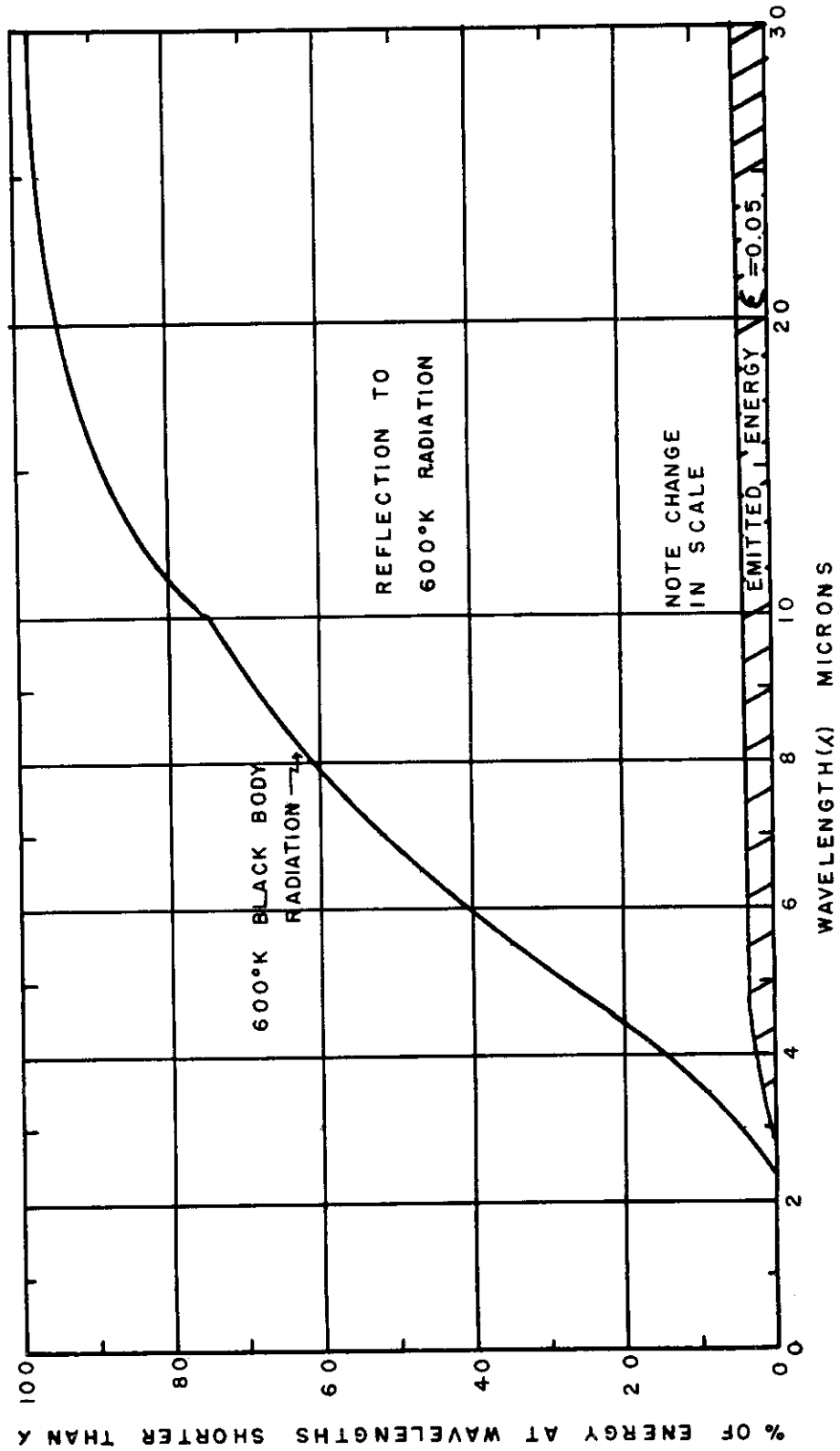


Figure 7 The Infrared Energy Absorption (or Emittance) of the Dark Mirror Coating

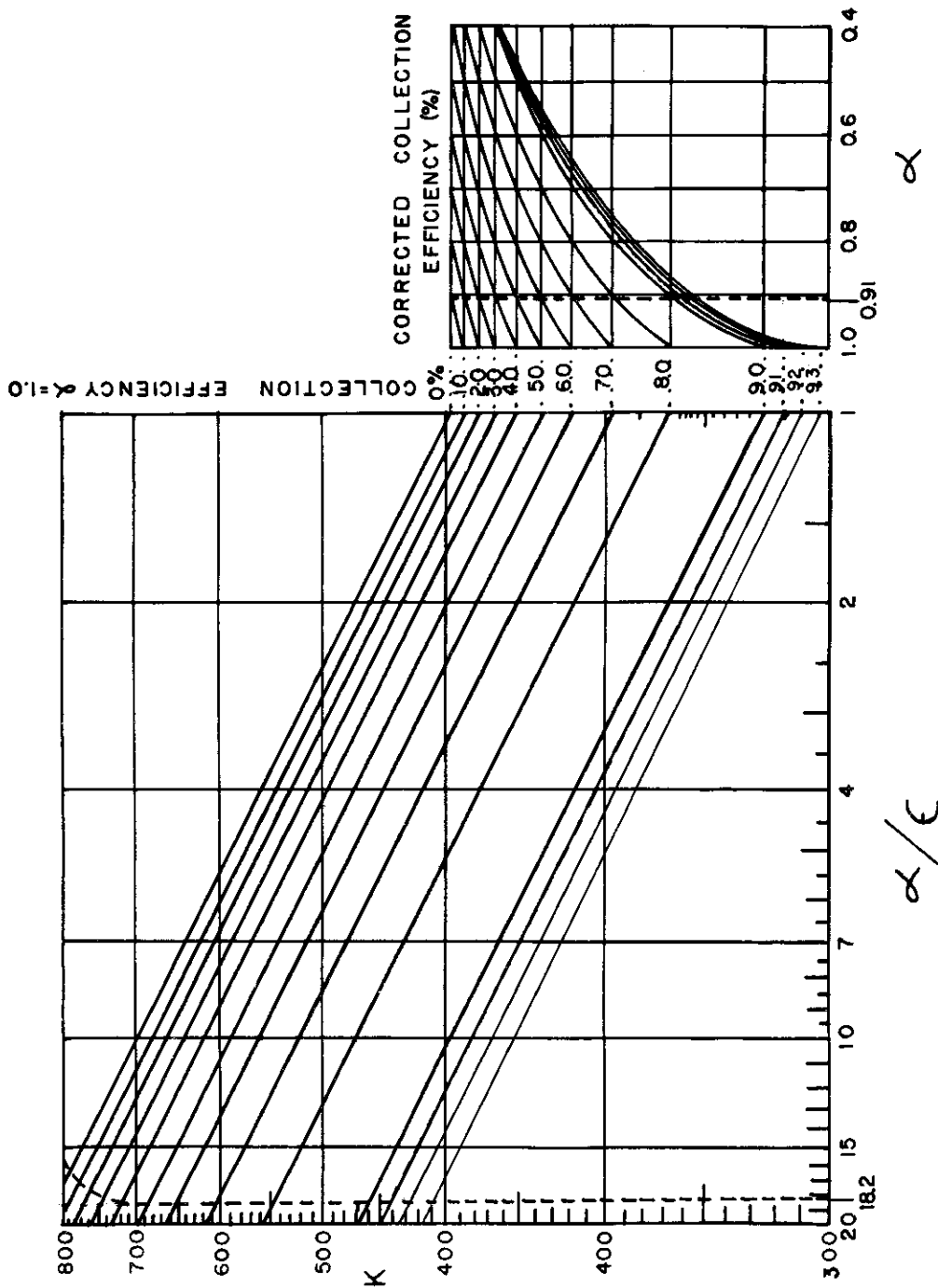


Figure 8 Application of the Coating Collection Efficiency Calculator to the Dark Mirror Coating

Contrails

Figure 9 summarizes the results of all the previous graphical study in a manner useful to the mechanical engineer for thermodynamic calculations. An aluminum alloy, 2024, was selected for comparison because it has a similar α/ϵ but a low α (0.4). This graph shows most clearly the fallacy of using α/ϵ as the sole criteria of coatings for solar power systems.

V. FUNDAMENTALS OF ENERGY ABSORPTION AND REFLECTION

Before one can design selective coatings, an appreciation of the fundamentals of energy control is necessary. Table II outlines the tools available for energy control. This table sets forth most of the important techniques of energy control. However, the reader should be aware that there are other radiation effects such as positive hole migration in semiconductors and Restrahlen reflection associated with vibrational absorption. These latter effects are relatively insignificant in practical coating materials as compared with the primary forms of energy conversion listed.

TABLE II

FUNDAMENTALS OF ENERGY CONTROL

A. Absorption

1. Electronic Transitions
2. Bond Vibrations
3. Optical Interference
4. Multiple Reflections - Cavities

B. Reflection

1. Metallic Reflection
2. Fresnel Reflection

Smooth Films

Light Diffusing Films

A. Energy Absorption

The primary method of energy absorption in the ultraviolet, visible and near infrared is due to electronic transitions to excited states. The materials undergoing the electronic transitions are termed chromophores, color bodies or stains. For the absorbed radiation to be converted to heat, the excited electron must give up its energy as molecular vibrational energy, rather than fluorescing or phosphorescing. Electronic transitions are generally limited to wavelengths shorter than

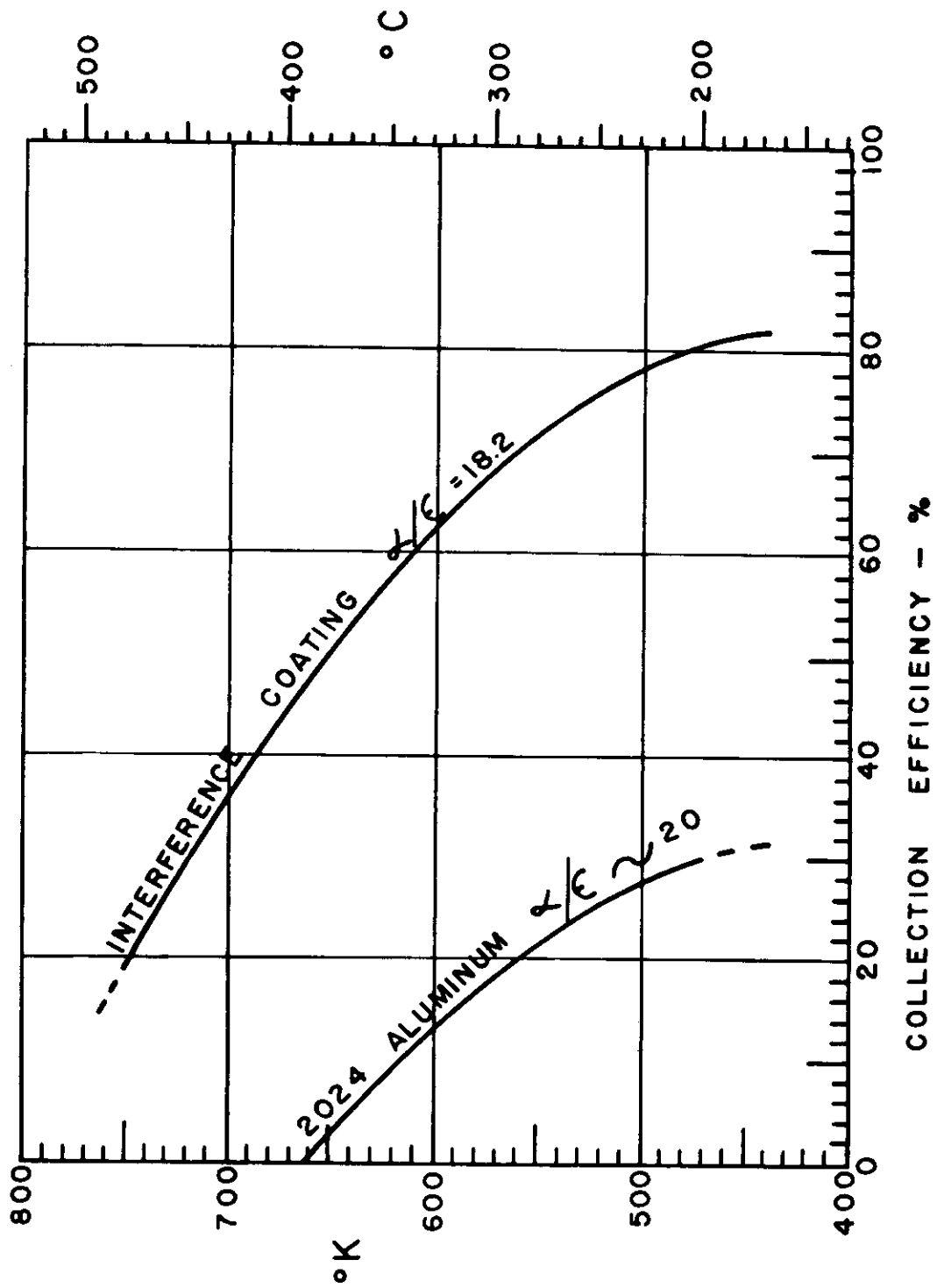


Figure 9 Coating Collection Efficiency vs Temperature

Contrails

2 microns so they do not take part in the thermal radiation from a surface except at very high temperatures. Since most electronic transitions involve large energy gaps (2 ev or more), the temperature of the coating has little effect on these transitions. For this reason the absorption of solar energy (94% shorter than 2 microns) will also remain almost constant with temperature. Where there is an effect, it is generally a minor increase in absorption due to a reduction in molecular symmetry which increases the probability of the electronic transition. Crystal structure changes at high temperature can also cause some change in energy absorption.

Except in highly doped semi-conductors and other special cases, energy absorption beyond 2 microns is primarily due to vibrational resonance between nucleous of a molecule and between molecular groups. It is this absorption by the bound electrons that is primarily responsible for heat transfer at temperature below the dissociation point of organic and inorganic materials. Organic materials exhibit the strongest vibrational absorption and conductive metals show very little absorption. Semiconductive metals and many metal halides are transparent to much of the infrared. Other inorganic compounds show intermediate to high absorption.

Absorption by optical interference occurs when light is reflected 90° out of phase from successive layers of a multilayer coatings. This can be best accomplished by alternating thin layers of metals and dielectrics. By proper selection of materials, it can be used to give narrow band or broad band absorption of light.

Since all materials have some absorption for light, a ray which is reflected many times will ultimately be totally absorbed. This is the principle of the black body cavity used as an emittance standard. It is also the explanation given for the light absorption of a rough or porous surface. However, some porous surfaces absorb only short wavelength light while reflecting long wavelength light. The popular theory for this phenomenon is that the pores are smaller than the wavelength of the reflected light. If this is true, the pores could be tailored to absorb only short wavelength light.

B. Energy Reflection

The reflection of infrared energy by metallic materials is caused by the interaction of light with the conduction electrons. If the conduction electron remains mobile during irradiation, it will be a perfect reflector, e.g. metals in the superconducting state are perfect reflectors. If there is an interchange of electrons between bound and conducting states, absorption will result. The reflection then becomes a function of the life time of the electron in the conducting state as is the electrical resistance. Mathematically, the reflection is given by the following relationship:

$$R_{\lambda} = 1 - \frac{2}{\sqrt{\sigma T}} = 1 - 0.365 \sqrt{P/\lambda}$$

Contrails

where:

$$\begin{aligned}\sigma &= \text{conductivity} \\ T &= \text{period} = c/\lambda \\ \rho &= \text{resistivity in ohm-mm} \\ \lambda &= \text{wave length in microns}\end{aligned}$$

This equation holds fairly well at wavelengths greater than 2 microns.

Fresnel reflection is a term, applied to the normal reflection from the surface of a dielectric. It varies with the index of refraction (n) as follows:

$$R = \frac{(n-1)^2}{(n+1)^2}$$

While the normal reflection of a single layer is not high, multiple layers can give reflectances exceeding 99%. These layers would normally be applied at $\lambda/2$ thickness for minimum absorption.

Light diffusing materials, such as white paints, foams and emulsions work on a similar principle, except that orientation of the reflecting particle is random. The total reflectance of some light diffusing materials, such as magnesium oxide smoke, can reach 97 to 99%. However, it is difficult to exceed 95% with pigmented coatings.

Neither of the above techniques has ever been applied to obtain reflection at wavelengths longer than 2 microns. This is largely due to inadequate knowledge of compatible materials that might be combined to give high reflection.

VI. COATINGS FOR SELECTIVE ENERGY ABSORPTION

In order to get selective energy absorption, the coating or coating system must have high absorption for short wavelength light and high reflection (or low emittance) for long wavelength light. This may be accomplished in one coating or with two coats where the top coat is transparent to certain wavelengths. In this case the second coat can accomplish the absorption or reflection as required. Some of the techniques for combining coatings to obtain selective properties are outlined in Table III and illustrated in figures 10 to 14.

TABLE III

SELECTIVE ABSORPTION TECHNIQUES

- A. Using Metallic Reflection
 - 1. Electronic Transitions
 - 2. Optical Interference
 - 3. Porous Metals
- B. Using Dielectric Reflection
(With an Absorbing Undercoat)
 - 1. Light Diffusing
 - 2. Light Reflecting - Fresnel

A. Coating Systems Using Metallic Reflection

Since metals are generally better reflectors of infrared light than short wavelength light, it is inevitable that coating systems should be designed to take advantage of this property. As denoted earlier, metal reflection is closely associated with its conductivity. Therefore, only the highly conductive metals are useful where maximum reflection is required. Gold, silver, copper and aluminum are the best of the common metals. Metals such as iron, chromium, zinc and platinum are distinctly inferior in infrared reflectance; their emittance is too high.

A suitable topcoat material must have a high extinction coefficient for short wavelength light and high infrared transparency. This is illustrated in figure 10 and can be accomplished by a semiconductive material which is doped to have an absorption edge at about 1.5 microns. Several of the metal oxides, such as cupric oxide, have absorption edges in the near infrared also. Where these coatings are applied in thicknesses considerably less than a quarter-wave of the emitted energy, the infrared absorption is minimized. Since most semiconductive materials increase absorption rapidly at wavelengths longer than 10 microns, the coating must generally be less than 2.5 microns. The extinction coefficient for short wavelength light must be very high to get high absorption in a film less than 2.5 microns thick.

One method of getting high absorption in an extremely thin film is to use optical interference as an absorption technique, see figure 11. These films are formed by depositing alternate layers of metals and dielectrics in quarter-wavelength films for visible and near infrared light. As shown earlier, about 90% absorption can be obtained in a three layer film.

Another method of getting selective absorption is the use of a finely divided conductive metal as in figure 12. Gold smokes form loose

deposits of colloidal gold on a condensing surface and have very good selective properties. However, they are mechanically and thermally unstable. This might be rectified by incorporation of a finely divided transparent material to fill the voids in the colloidal metal surface.

B. Coating Systems Using Dielectric Reflectors

The thin film reflector shown in figure 13 appears the most practical dielectric system in that many pure compounds can be vacuum deposited in thin adherent films. Chemical deposition may also be possible in some cases. Many compounds, such as certain oxides and sulfides are not suitable for vapor deposition because they undergo reduction in the vapor phase to change the composition of the applied film. Elements and compounds involving group IV and VII elements are the most promising for the high index of refraction materials.

The problem with light diffusing dielectric reflectors such as the one in figure 14, is that of finding suitable and compatible materials. The organic materials that might be useful, polyethylene and polytetrafluoroethylene respectively, have relatively poor thermal resistance. Inorganic coatings, similar to porcelain enamels, may be possible but the formulator doesn't have many materials which are compatible with both the optical and physical properties required in the enamel.

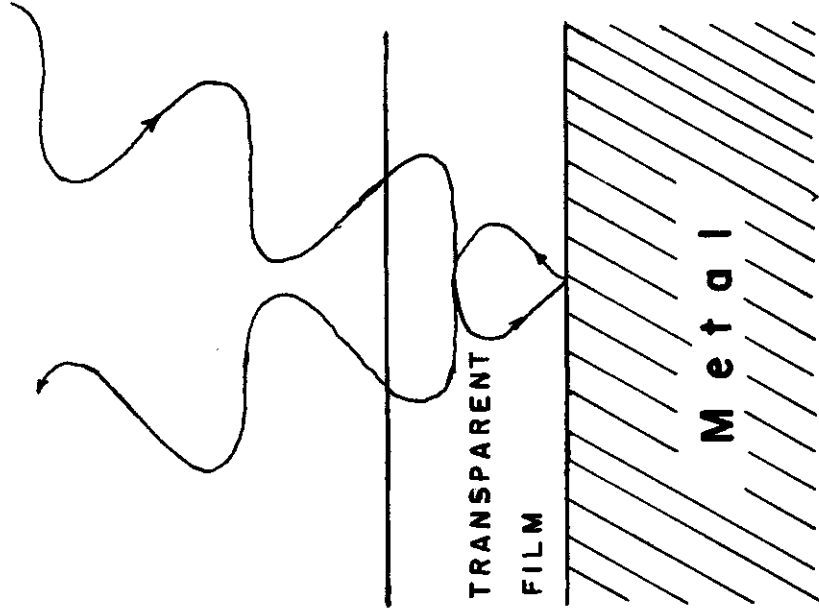
To be useful, dielectric reflectors must reflect only in the infrared. If they do not absorb short wavelength light, an absorbing undercoat must be used. For the light to reach this undercoat, the index of refraction of the two phases must be about the same for short wavelength light.

VII. CONCLUSIONS

1. Optical studies show that the solar absorption α must be considered on an equal basis with the absorption to emittance ratio (α/ϵ).
2. There are several approaches to obtaining selective coating systems using metal and dielectric reflectors (with dielectric absorbers), and only a few of these approaches have been partially explored.

LONG λ

Metallic Reflection



SHORT λ

Electronic Absorption

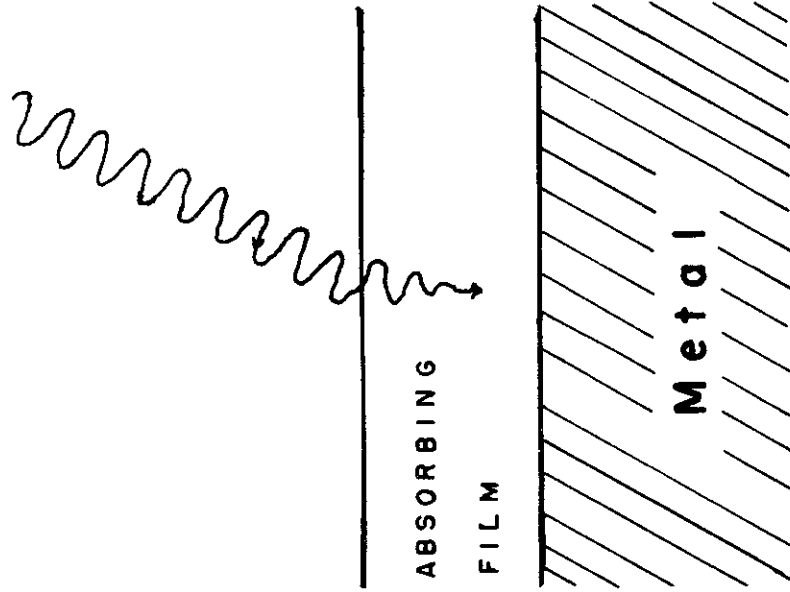


Figure 10 Absorption by a Selective Black

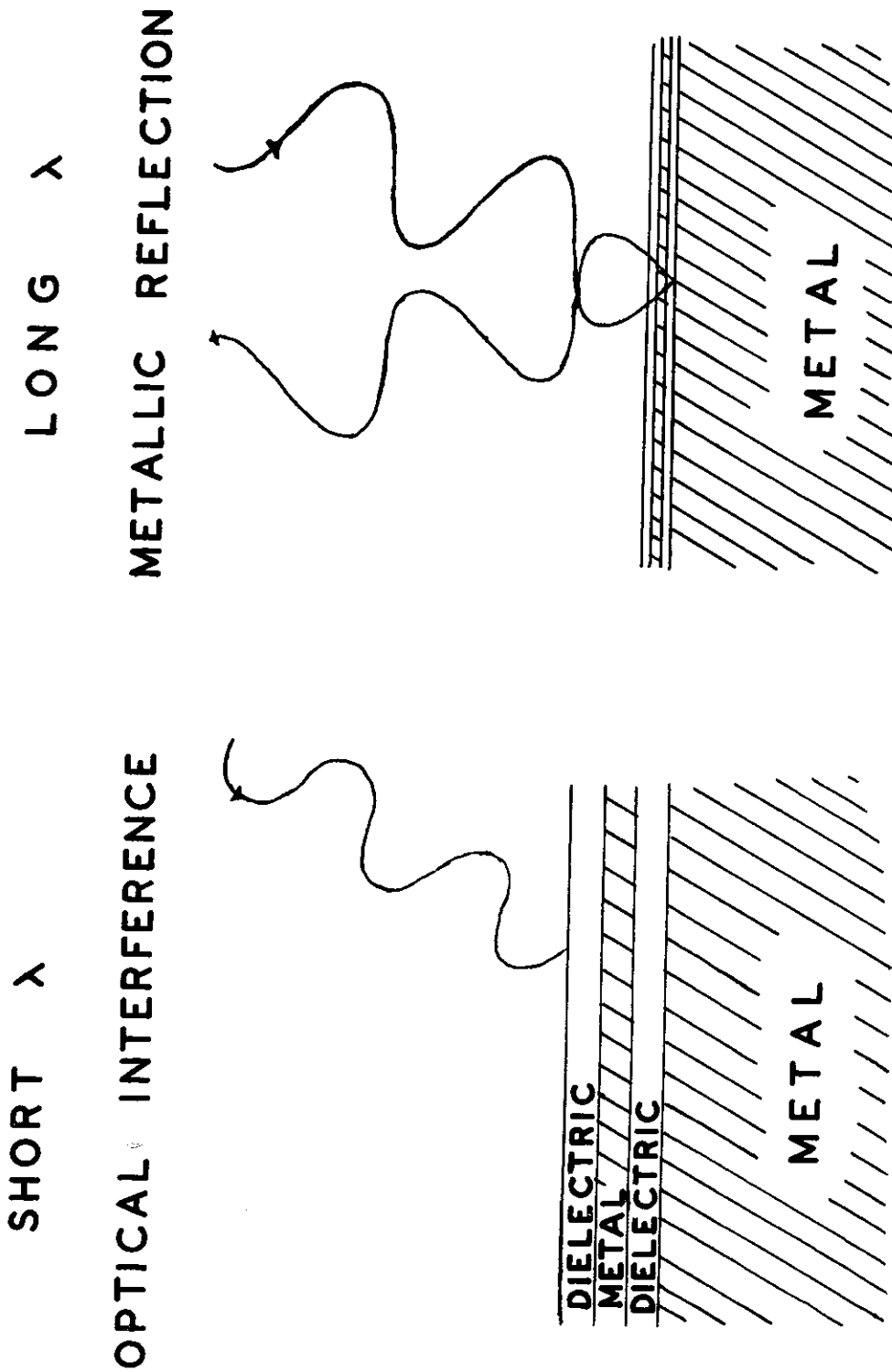


Figure 11 Absorption by Optical Interference

SHORT λ LONG λ

Cavity Absorption Metallic Reflection

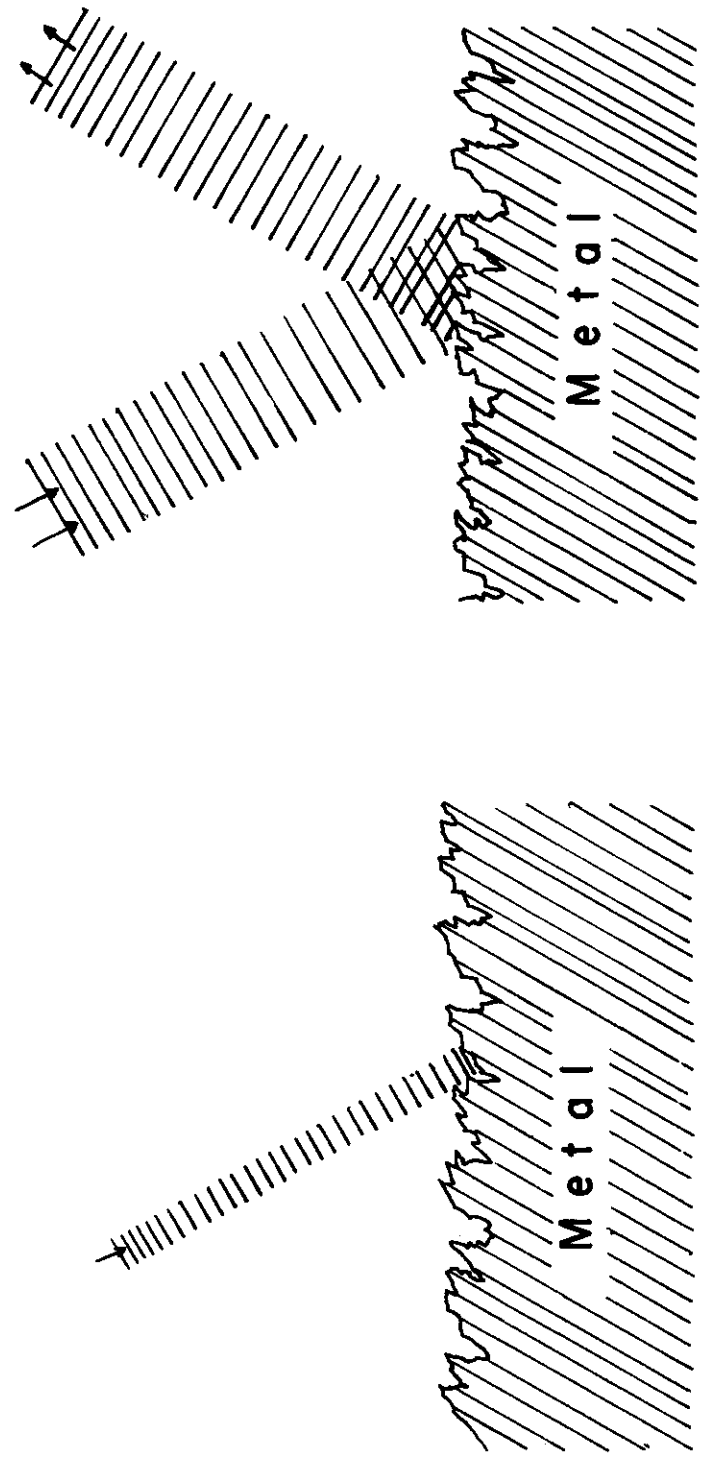
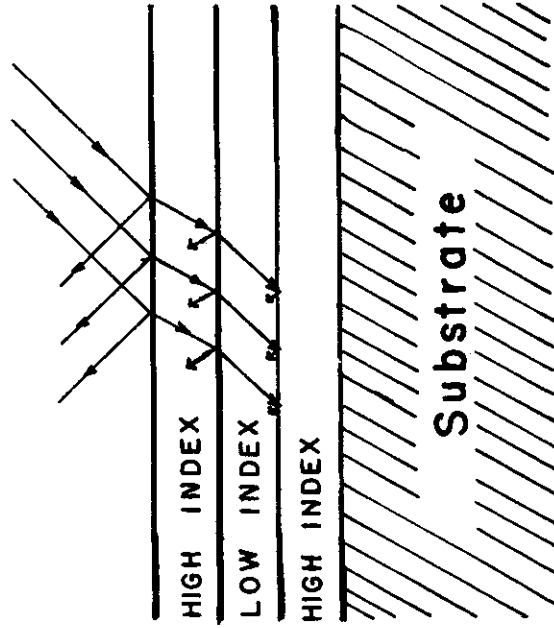


Figure 12 Absorption by a Microporous Surface

LONG λ

Dielectric Reflector



SHORT λ

Black Undercoat

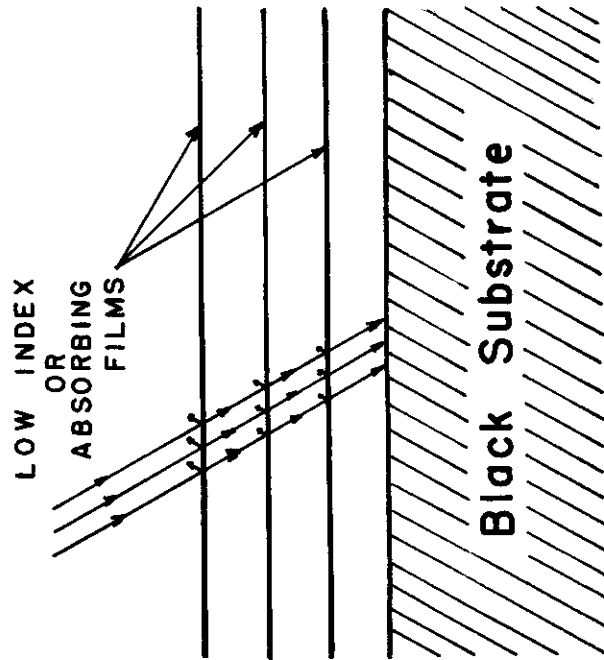


Figure 13 Dielectric Reflector

SHORT λ LONG λ
Black Undercoat Diffuse Reflection

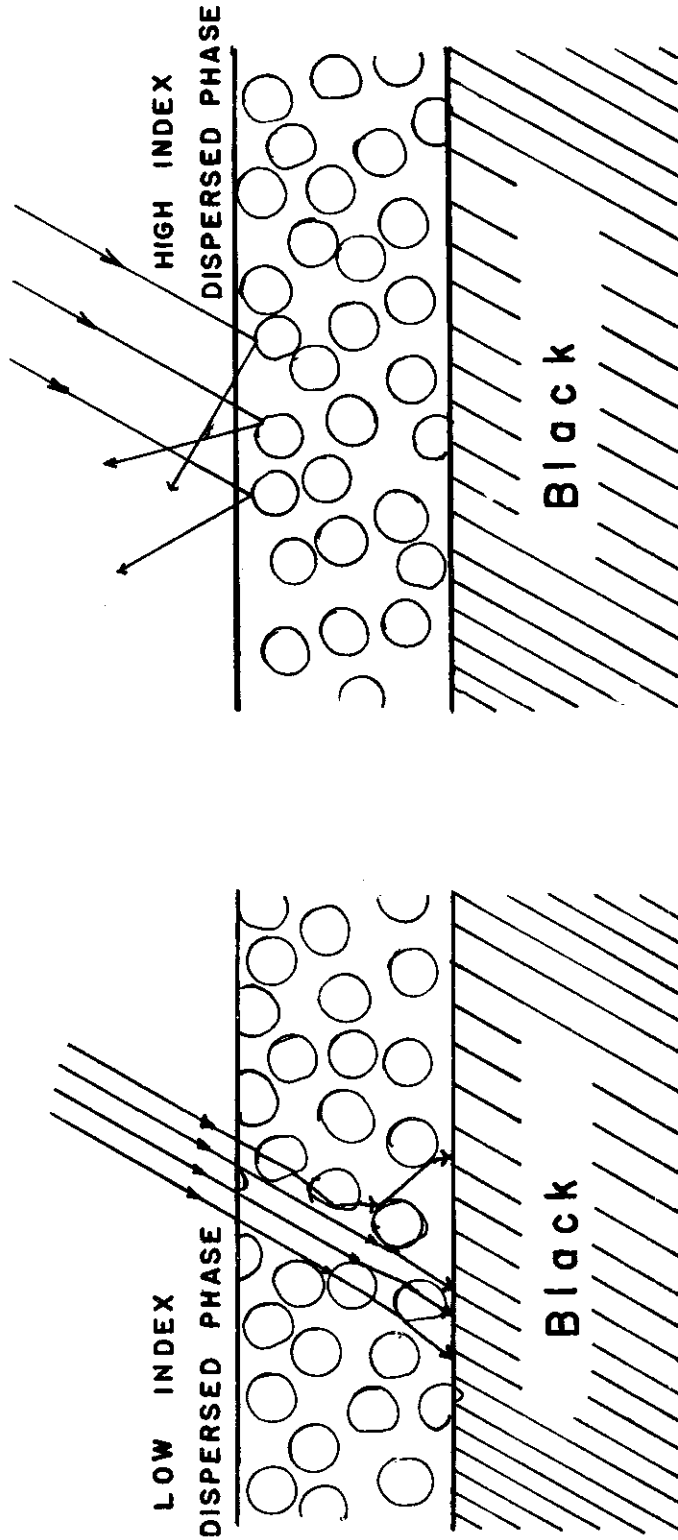


Figure 14 Infrared "White" Reflector