Title
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THE USE OF COATINGS FOR ENHANCED SOLAR THERMAL ENERGY COLLECTION

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DISCLAIMER

THE USE OF COATINGS FOR ENHANCED SOLAR THERMAL ENERGY COLLECTION

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ABSTRACT

For efficient and economical utilization of solar energy various types of coatings and preparations can be used for solar collectors and for the window systems in buildings. In this study several kinds of commercial and research coatings are discussed in detail for this application; selective, moderately selective and non-selective black absorber coatings are reviewed and tabulated. Both heat mirror and cold mirror coatings are considered for applications where heat and light need to be separated and trapped. Also, antireflective films for glass covers and windows are analyzed. For many of these coatings, detailed reflectance, emittance, and thermal stability data are presented. Since selective absorbers offer high solar absorption with low infrared emittance, these surfaces can take advantage of various optical absorption methods including light trapping, particulate coatings, semiconductor-metallic layers, multilayer films, quantum size effects and also intrinsic absorption. Non-selective and moderately selective absorbers consist of black paint, chemical conversion coatings, electroplated and anodized coatings. Cold mirror coatings perform like good visible radiation reflectors and exhibit transmission in the infrared. On the other hand, heat mirrors show an opposite effect, high transmission in the visible with good infrared reflectance. The results of this study revealed many inexpensive and promising

low temperature (150°C-300°C) absorber coatings. For higher temperature use there are a few highly engineered coatings or paints which will withstand 500°C or more. All of these coatings play a vital role in the effective utilization of solar energy.

1. INTRODUCTION

If we are to utilize solar energy for specific purposes or end uses we need to know the role coatings can play and especially when they are a crucial and important consideration in terms of energy collection and cost effectiveness. Also, we should know how various coatings perform, the types available, projected cost and potential areas of application. Then it is important to point out problems associated with usage of particular coatings. We would like to predict how the use of coatings can create some impact upon the various sectors of energy consumption. Of course, there are many questions; some can be partially answered but most are too complex to be dealt with here as they depend upon the whole spectrum of energy production, availability, and consumption in dynamic interaction with social, political and environmental considerations.

The following study is aimed at the technical reader who is concerned about the properties of coatings for the collection of solar thermal energy. Photovoltaic coatings will not be reviewed at this time. The type of coatings of major concern are selective and non-selective absorbers, heat mirror, cold mirror and antireflective coatings. These coatings will be reviewed and analyzed in terms of potential widspread application. This study will give the readers a "feel" for the use of coatings in the perspective of their usefullness and inherent limitations. The scope of this report is to put forth data about commercially available or potentially available surface coatings and to study them in the context of application, collector design, and ends use temperature.

It is important to review briefly the current applications of coatings. For non-concentrating swimming pool heaters and fairly low temperature solar water and air heaters, non-selective paints are in use. Selective surface coatings play an important role when temperatures are required in the vicinity of boiling water because radiative losses become large at these temperatures. Heat mirror coatings also are useful in this range. At higher steam temperatures, evacuated tubes and selective absorbers are used to cut down on increasing convective and radiative losses; usually, these collectors are of the concentrating design. Antireflection films are ordinarily necessary for medium technology collectors in the realm of selective absorbers where the reflection losses can be quite significant. Cold mirror coatings have applications for the control of greenhouse and dwelling temperatures. Heat mirrors are also used for dwelling temperature control.

Many of the various selective and non-selective surfaces can be applied to a variety of materials. Common absorber plate materials are steel, copper and aluminum and to a lesser degree, glass and stainless steel have been employed. Heat mirrors, cold mirrors and antireflection coatings are usually applied to either glass or various polymer collector covers and window systems. However, antireflection coatings can be used directly on semiconductor absorber coatings.

The following sections will reveal details about the usage of various materials and the combination of their physical properties to obtain these very useful coatings.

2. DEFINITIONS OF OPTICAL PARAMETERS

In most cases reported, for both selective and non-selective coatings, reflectance measurements are used to derive both absorptance ($a_w(m,p)$) and emittance ($e_w(m,p)$) of the various materials. At times, however, emissometers are employed to measure emittance. Some investigators use direct beam spectral reflectance measurements to characterize their samples, while others use hemispherical spectral reflectance and calorimetric method. On the other hand, many do not even report the techniques used to obtain their values. As a result, discrepancies due to equipment and techniques are common and absolute values for any one particular surface are not well defined.

Absorptance is the fraction of incident energy absorbed by the surface at a given wavelength (w) and direction (m,p) to that surface. Emittance is defined as the ratio of the emitted total energy intensity from a surface in the direction (m,p) to the blackbody intensity, where both the surface and blackbody are at the same temperature.

In practice, both absorptance and emittance are integrated values. Integrated absorptance (a) is the average absorptance at each wavelength, weighted according to the solar energy intensity distribution. Net emittance (e) is calculated by taking the average emittance at each wavelength weighted according to the blackbody intensity distribution (corresponding to the operating temperature of the surface). The ratio a/e serves as a figure of merit, with non-selective surfaces exhibiting $a/e = 1$ and selective surfaces $a/e > 1$.

3. SOLAR SELECTIVE ABSORBERS

In general, a selective absorber, sometimes called a selective surface, is a material or coating which exhibits optical selectivity; that is, optical properties which vary greatly from one spectral region to another. The optical properties of usual interest are reflectance, transmittance, absorptance, emittance, index of refraction and the extinction coefficient. In the field of solar energy a selective absorber efficiently captures solar energy in the high intensity visible and the near infrared spectral regions while exhibiting poor infrared radiating properties. Accordingly, a selective coating will absorb and retain a high amount of energy from the sun while a non-selective surface, such as an ordinary black paint, will lose much of its absorbed energy by reradiation. For optimum efficiency the solar absorber should possess the maximum possible absorptance in the solar spectrum while maintaining a minimum infrared emittance. An example of this effect is shown in Fig. 1. The blackbody spectra shown in this figure represents the ideal distribution of energies radiated by the selective absorber operating at a specific temperature. Also, in this figure the wavelength distribution of the solar air mass 1 spectrum is shown for comparison. Solar selectivity can be obtained by a variety of methods. These techniques are outlined in the following tabulation:

1. Intrinsic solar selective materials.
2. Optical trapping by surface cavities or physical wavelength discrimination.
3. Particulate coatings, composite film
4. Absorbing semiconductor/reflecting metal tandem.

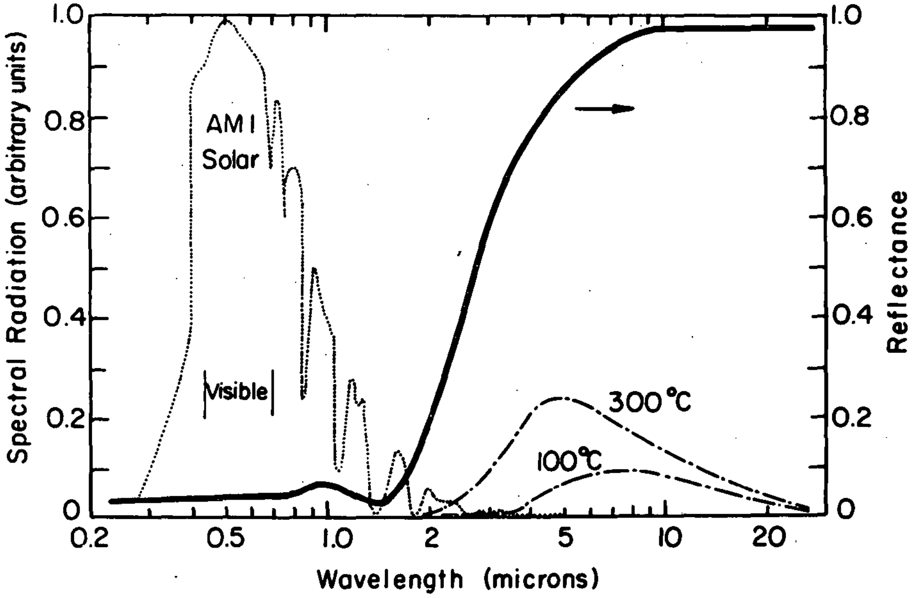

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Fig. 1. Wavelength relationship between a characteristic solar selective surface in terms of reflectivity, to that of the solar energy (AM1) and blackbody spectra (100°C, 300°C).

5. Multilayer thin films.
6. Quantum size effects.

Many actual selective coatings consist of combinations of the above groups. For example, a surface may exhibit both mie scattering and semiconductor/metal tandem properties. In the sections to follow, these basic methods in obtaining selectivity will be discussed and exemplified by selected current research and commercial processes. A summary table (Table 2) will be presented at the end of this section for comparison of the various absorber types.

3.1. Intrinsic Absorbers

There is no intrinsic material occurring in nature which exhibits ideal solar selectivity. There are, however, materials that approximate the required solar selective characteristic. By study of these unusual materials it may be possible with the knowledge obtained to synthesize new or improved intrinsic selective absorbers. To reach this goal it is necessary to understand complex electronic structure and its influence on optical properties. If such an understanding is obtained then it would be possible to design absorbers outright by using solid state physics.

Two categories of materials are good candidates for intrinsic absorbers because they already exhibit at least one desirable absorber characteristic. They are transition metals and semiconductors. Only after great solid state modification could each one serve as an intrinsic absorber. In general, metals exhibit a plasma edge (see Fig. 2) too early in the solar spectrum to be good absorbers. By creation of internal scattering centers it is possible to shift this plasma frequency towards

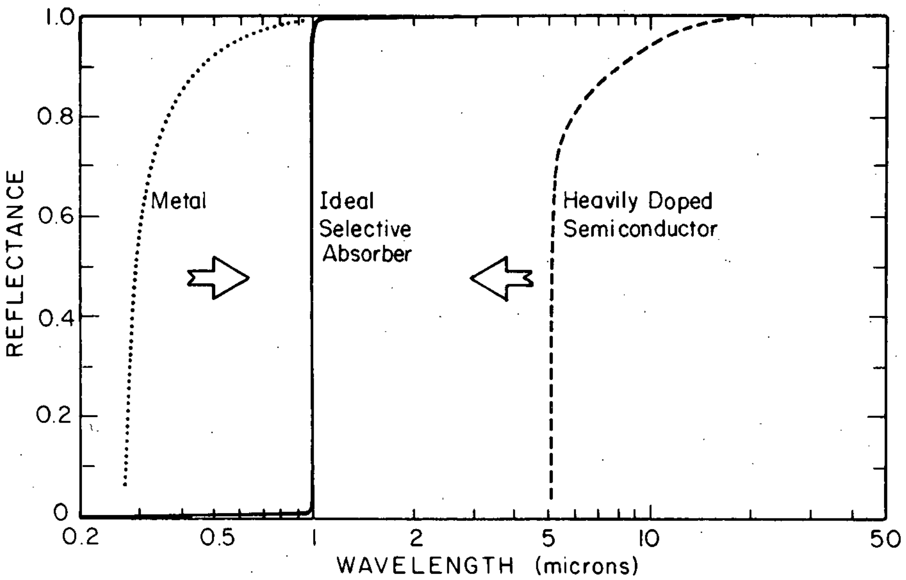

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Fig. 2. Reflectance of an ideal selective absorber compared to that of an idealized metal and heavily doped semiconductor (after Seraphin [83]).

the infrared. An example is MoO_3 doped Mo developed by Seraphin and Associates [83] as shown in Fig. 3. Pure tungsten is shown for comparison; it is one of the most wavelength selective metals. A semiconductor exhibits the opposite problem. By making a semiconductor highly degenerate it may be possible to suppress its plasma frequency in the infrared, making it a poor emitter then. Unfortunately, these adjustments to atomic structure are not as simple as portrayed; there are many subtleties and unknowns involved. Further considerations of these details and conjectures are discussed by Seraphin [3,83,84] and Ehrenreich [1]. In the following discussion unusual materials will be looked at, as they possibly may provide insights into the creation of truly intrinsic absorbers, not to mention advancement of the field of solid state theory applied to optical materials design.

Most intrinsic absorbers are transition metal oxides, sulfides, nitrides or carbides. An example of a carbide is hafnium carbide, HfC, shown in Fig. 3, along with the semiconductor, Cu_2S, a tandem absorber material.

Most semiconductors exhibit transmittance in the infrared energies so metals are employed to provide a low infrared emittance. Three transition oxides clearly indicating selectivity are shown in Fig. 4. All of these oxides exhibit optical transitions too early in the energy spectra, as depicted by the bracketed visible region. If, by some materials science means these spectra could be shifted to longer wavelengths, an ideal selective absorber might be created. The distinct feature of these oxides, as noted by Ehrenreich et al. [1], is an incompletely filled d-shell of the metallic ion. When this ion is

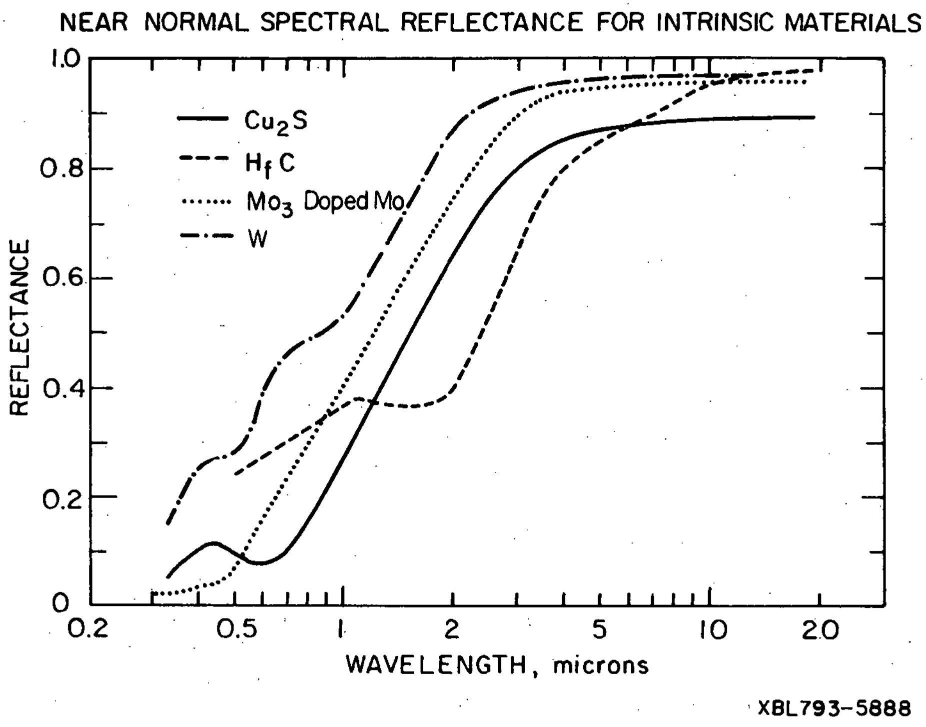

Fig. 3. Spectral reflectance for intrinsic materials Hafnium carbide, metallic tungsten and MoO_3 doped Mo, B. O. Seraphin [1,83], and semiconductor Cu_2S, Meinel and Meinel [2].

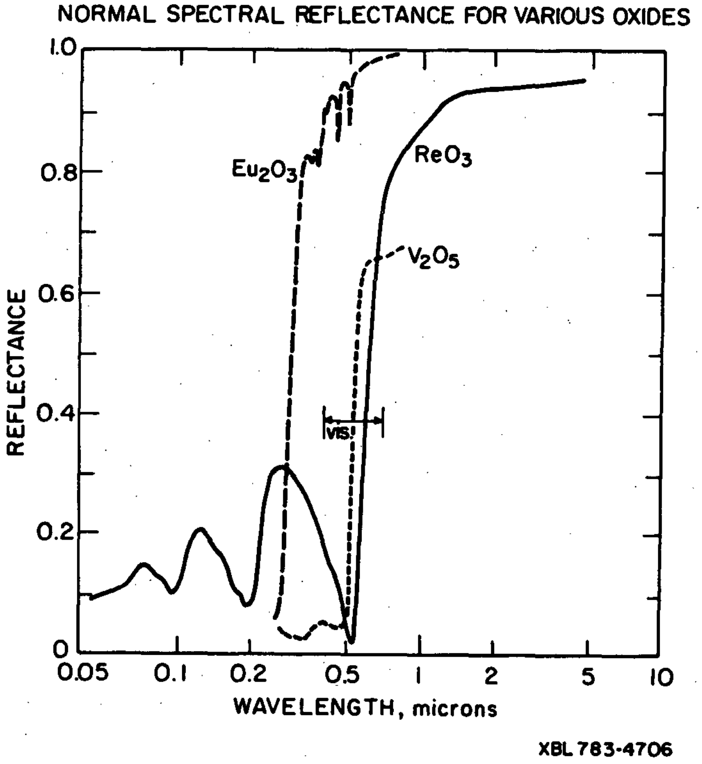

Fig. 4. Spectral reflectance of various oxides compiled by Touloukian et al. [4] showing intrinsic selectivity for dieuropium trioxide, rhenium trioxide single crystal and divanadium pentaxoide.

combined with oxygen, these electrons become localized, resulting in this optical property. Also under speculation by Seraphin [3] is the addition of sodium to tungsten trioxide, WO_3, resulting in a metallic oxide like ReO_3 [1]. Another material is lanthanum hexaboride, (LaB_6) a transmitting selective material exhibiting 85% transmission in the visible and 90% reflectance in the infrared. This material might have a heat mirror application if it were overcoated with a dielectric layer which would cut down the visible reflectance. To further develop these intrinsic absorbers one must investigate the band structure of these various materials and others related to them. It is also necessary to understand the materials science of these materials and its effect upon the resulting optical properties. Another important consideration is to determine the influence of structural imperfections, such as dislocations, vacancies and interstitials, upon the optical properties of these materials.

3.2. Optical Trapping

A common technique used to obtain optical trapping of energy or wavelength discrimination is surface roughening. It is possible to produce a surface which would appear rough and absorbing to visible energy while appearing mirror like and poorly emitting in the infrared. An important point to note here is that the unroughened material would not have to exhibit a high intrinsic absorption coefficient in the visible region and because of this, metals roughened by some technique might make excellent optical trapping solar absorbers. Nearly ideal surfaces have been produced by chemical vapor deposition (CVD). The CVD deposition of rhenium by Seraphin [7] and tungsten by

Cuomo et al. [8] results in a dendritic structure. These dendrites appear as conical needles or whiskers. The dendrite forests absorb high energy solar radiation by the geometry of multiple absorption and reflection as depicted in Fig. 5. The sum of these absorptions are very high with respect to the incoming radiation, although a single absorption might be quite low. In the thermal infrared region the wavelengths of energy are much larger than the dendrite spacings; the surface appears fairly smooth, acting like a poor radiator of energy.

The tungsten dendrite structure is made up of three distinct regions. The base is a continuous polycrystalline layer exhibiting a high degree of texture. On top of this layer are two different sizes of dendrites. One group averaged 10 microns high with a spacing of 5 microns, while the layer dendrites measured 40-60 microns tall with 40-60 microns spacing according to Cuomo et al. [7] This dual forest probably is responsible for the wide range of optical absorption, anomalous to a broad band absorption filter. Pettit et al. [59] found that anodization can improve the optical selectivity of the tungsten surface. A potential advantage with the dendrite absorber is that it can be used at an elevated temperature for highly concentrating collectors or high temperature steam generators. Most types of selective surfaces cannot withstand high temperatures greater than 350°C.

A fairly random dendrite coating can be formed directly on collector plates by reacting laminated metal layers in an exothermic atmosphere, was performed by Santala and Sabol [9]. The resulting surface for a fully formed $NiAl_x$ layer can be viewed in Fig. 6. There is a listing

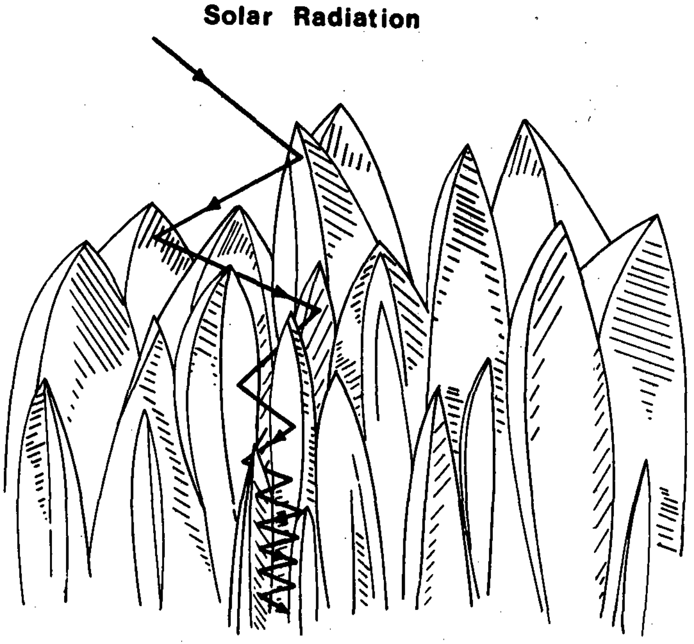

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Fig. 5. Schematic representation of a dendritic selective surface. Incoming radiation can average up to fifty reflections before being completely absorbed.

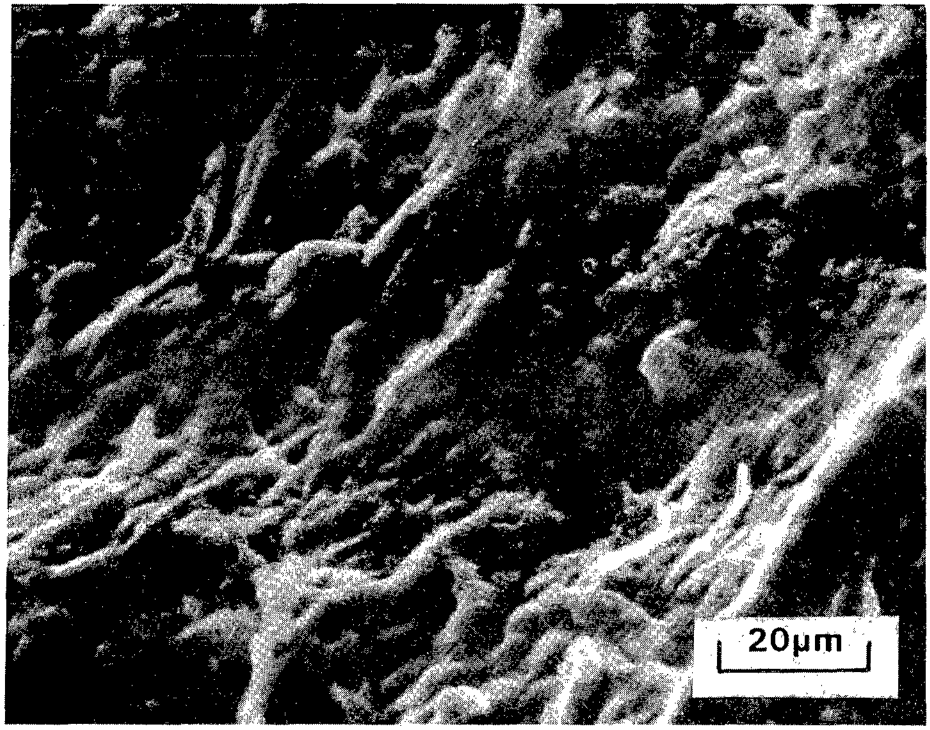

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Fig. 6. This surface shows solar selectivity by exhibiting a dendritic fine structure of the size order of the wavelengths absorbed for the 4022 Aluminum/201 Nickel absorber. This surface was formed by reacting metallic laminated layers bonded directly to collector panels. (Photo credit: T. Santala and R. Sabol, Texas Instruments).

in Table 1 of the absorptance and emittance properties of these various absorber types. The most successful of the intermetallic surfaces is the aluminum-nickel surface which consist of visible wavelength size cavities. In general, optical trapping surfaces are in the developmental stage so many pertinent properties of the materials and techniques are unknown for immediate solar collector application. Various optical trapping surfaces are listed in Table 1 along with their solar properties.

Reducing the size of surface roughening to the order of the wavelength of energy desired to be absorbed, can increase the net absorptance of the absorber, but it can at the same time increase the infrared emittance. The amount of increased emittance is related to the micro-roughness and crystallite size. The net effects of micro-roughness can be quite complex for a realistic absorber. At very fine surface roughness there is a trade-off between what is known as reflective scattering, due to cavities, and that of resonant scattering which is dependent upon the material and its morphology in the sub-wavelength size range. In the following section on particulate absorbers the details of resonant scattering will be discussed at length.

3.3. Particulate Coatings

There are two different mechanisms of absorption for particulate coatings, reflective and resonant scattering. Reflective scattering is obtained purely by the geometry of imbedded surface particles. These particulate surfaces appear to be wavelength selective by purely geometric multiple reflection means. Resonant scattering, on the other hand, deals with both the size and optical properties of the

Table 1. Optical trapping surfaces.

Type	a	e	a/e	Structure
Tungsten dendrite (IBM)	0.99	0.26-0.3 (550°C)	3.8-3.3	Aligned Dendrites
Aluminum--Steel (TI)	0.99	0.55 (26°C)	1.8	Random Dendrites
Aluminum--304 Stainless Steel (TI)	0.89	0.47 (26°C)	1.9	Random Dendrites
Aluminum--Nickel (TI)	0.94	0.30 (26°C)	3.1	Porous Cavities
4022 Al--201 Nickel (TI)	0.97	0.21 (26°C)	4.6	Porous Cavities
Aluminum--430 Stainless Steel (TI)	0.98	0.51 (26°C)	1.9	Random Dendrites
Nickel dendrite (LASL)	0.95	0.6 (100°C)	1.6	Rounded-aligned dendrites
On aluminum		0.71 (100°C)	1.3	

Source: Refs. IBM [7], TI [9] and LASL [85].

particles and surrounding media. The Mie effect and Maxwell-Garnet theory describe resonant scattering in an idealized way. These theories predict high forward scattering from particles much less than 0.10 of the wavelength of the incident enegy. Actually, both theories are inadequate in describing real systems of particulate selective absorbers which consist of complicated dispersions of metallic or semiconductor particles in dielectric or conductive matrices. suspension of metals such as chromium, copper, calcium and titanium can exhibit broad visible region resonance or absorption while appearing highly reflective or transparent in the infrared wavelengths. The exact frequencies of reflectance transition and absorbtion are controlled by the size, shape, distribution, and individual optical properties of the media involved. Characterization of a real system such as the quite promising electroplated black chrome surface is difficult, because it is hard to identify and control chromium particle size and shape and the exact matrix composition of an amorphous oxide phase (Cr_2O_3), investigated by Lampert [10]. Shown in Fig. 7 is an electron micrograph depicting small particles of chromium in the size range of 140Å imbedded in a chromium oxide host matrix. Also, this real surface shows reflective scattering by its surface, as seen in Fig. 8. Other investigators' such as Driver [11] and Pettit [12], have noticed this scattering in similar types of black chrome. The effect of substrate roughness and reflectance upon the properties of black chrome have been investigated also by Hogg and Smith [13]. This coating has been modeled by physical scattering theories by both Granqvist and Humderi [65] and Ignatiev et al. [63], although this coating appears to be much

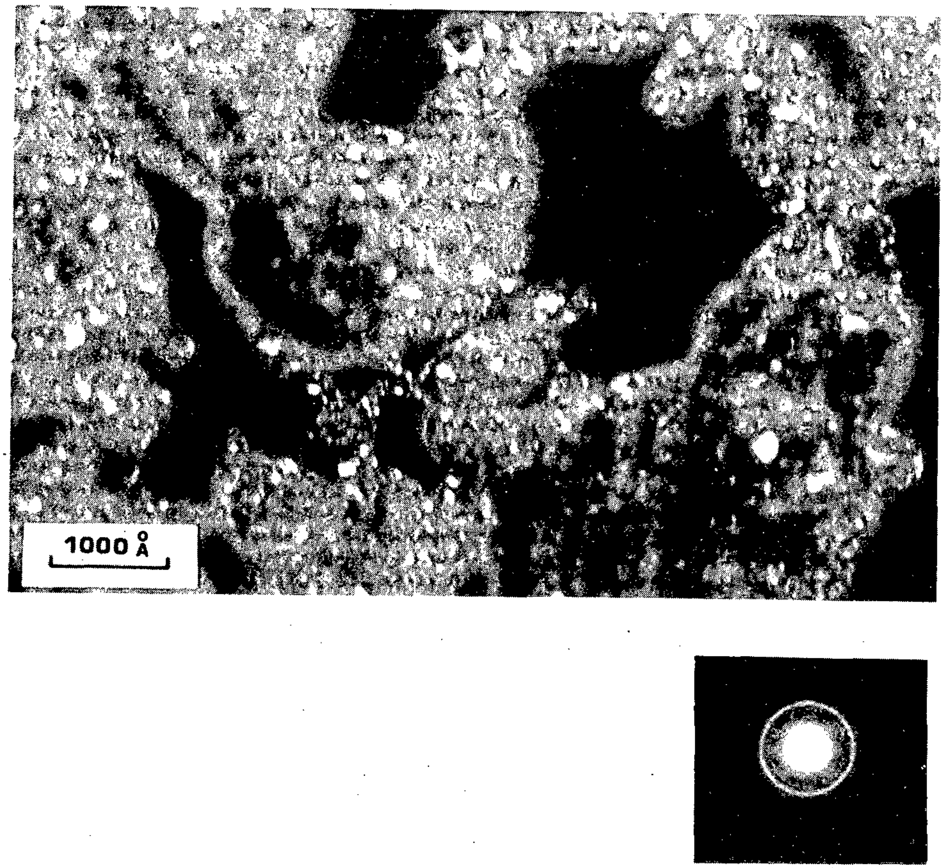

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Fig. 7. Agglomeration of chromium particles with matrix material viewed by transmission electron microscopy. This dark field shows metallic chromium particles as bright spots. Mean particle diameter is ~140Å according to Lampert [10].

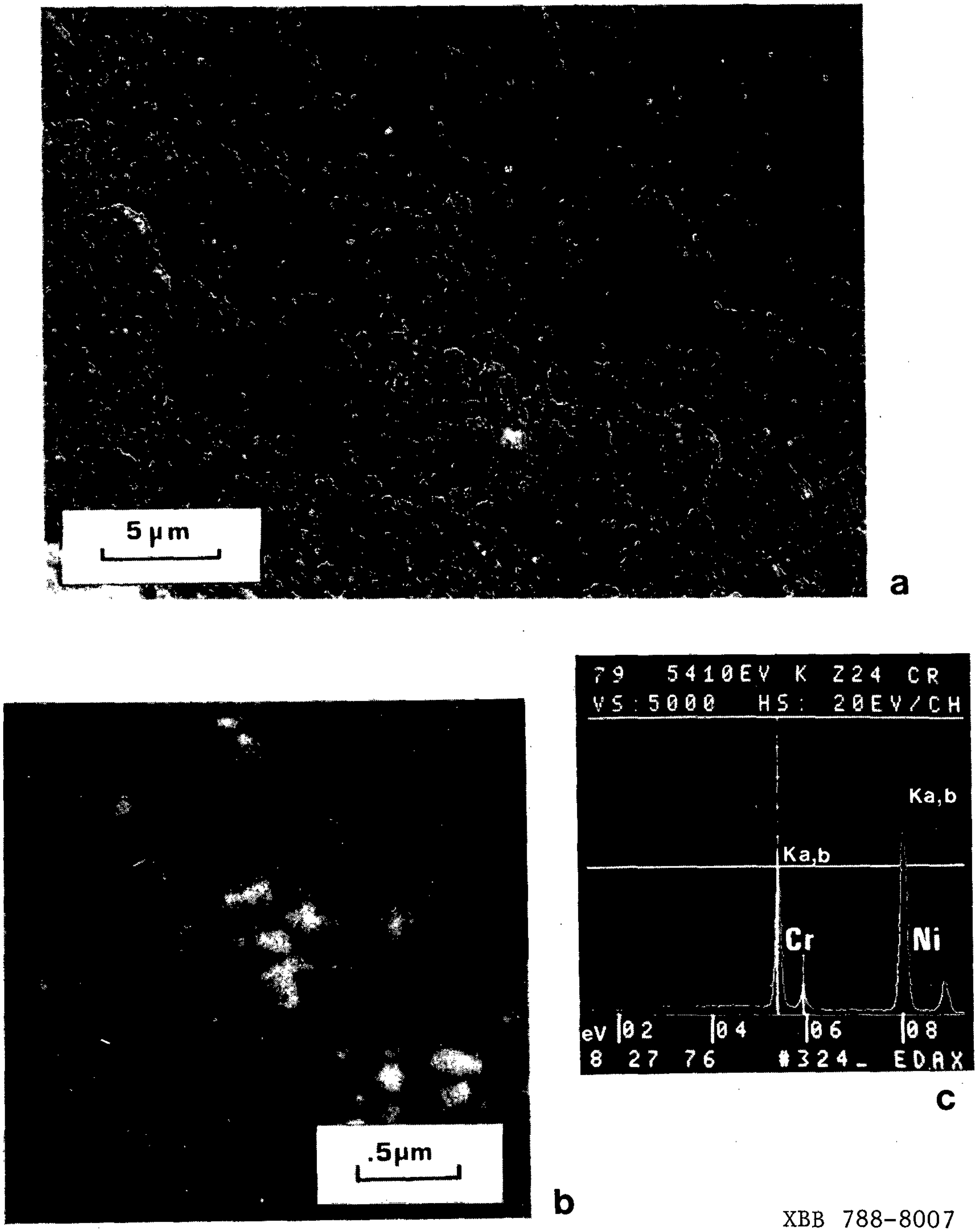

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Fig. 8. Black chrome on nickel plated copper examined by scanning electron microscopy by Lampert [10]. (a) Typical surface microstructure, (b) detail of particles, (c) EDAX of region (b), showing chromium and nickel as principal constituents.

more complex than models can easily describe. Reflectance values for various types of this successful coating by both are presented in Figs. 9 and 10. In Fig. 9 three types of electroplated black chrome are shown along with a cermet, made by Fan and Sprua [14], consisting of 29% chromium particles in a Cr_2O_3 matrix with crystallite sizes of the order 150Å. The cermet surface attempts to model the more complicated black chrome surface and shows that RF sputtering can yield a very selective chromium black. The effect of thickness variation on spectral reflectance for the LBL black chrome absorber can be seen in Fig. 10. By changing the thickness of the black chrome surface the optical transition can be adjusted as noted by McDonald [15,16] and Lampert [53]. The black chrome surface in many ways appears as a simple tandem absorber; the infrared spectral response does depend upon the properties of the base metal. A Tandem absorbers will be discussed in the following section.

Other particulate surfaces, made by Williams et al. [19], can consist of very fine semiconducting particles such as PbS imbedded in a silicon paint, brushed onto a metallic collector surface. These finely divided particles give a high degree of forward scattering to accomplish absorption as shown in Fig. 11. Tin particles, 400Å size, suspended in a MgF_2 matrix represent another successful system, made by Zeller and Kuse [20], which exhibits high visible opacity and infrared transparency. Shown in Fig. 11 are various types of particulate absorber films depicting optical transitions either in the infrared or of visible wavelength regions. The silicon powder absorber coating investigated by Warren [21] represents a novel method of producing

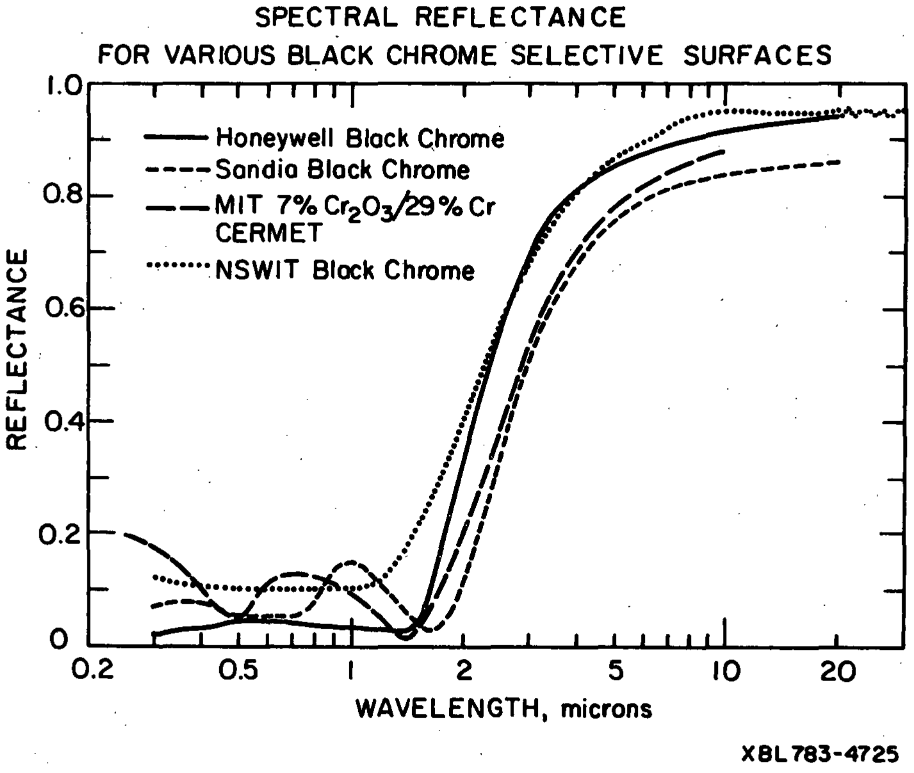

Fig. 9. Reflectance for different types of selective surfaces, including the Honeywell (Masterson et al. [17]), Sandia and New South Wales Institute of Technology (Driver et al. [18]) electroplated surfaces. The MIT cermet [14] is shown for comparison.

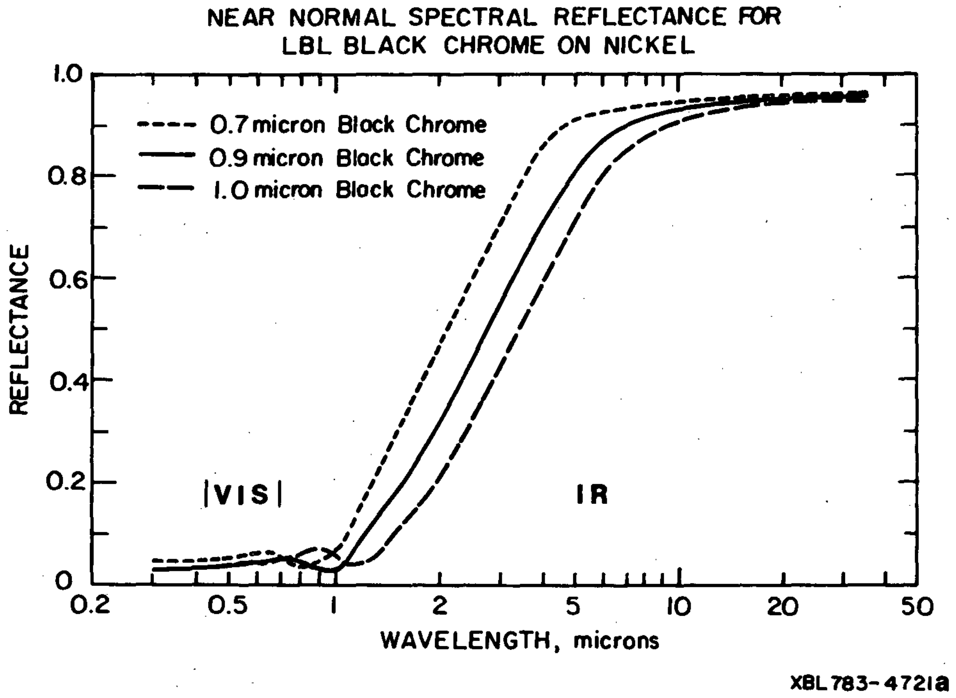

Fig. 10. Variation of hemispherical spectral reflectance with thickness for black chrome on nickel, Lampert [10]. Coating thickness was determined by plating bath parameters, as noted by McDonald [16].

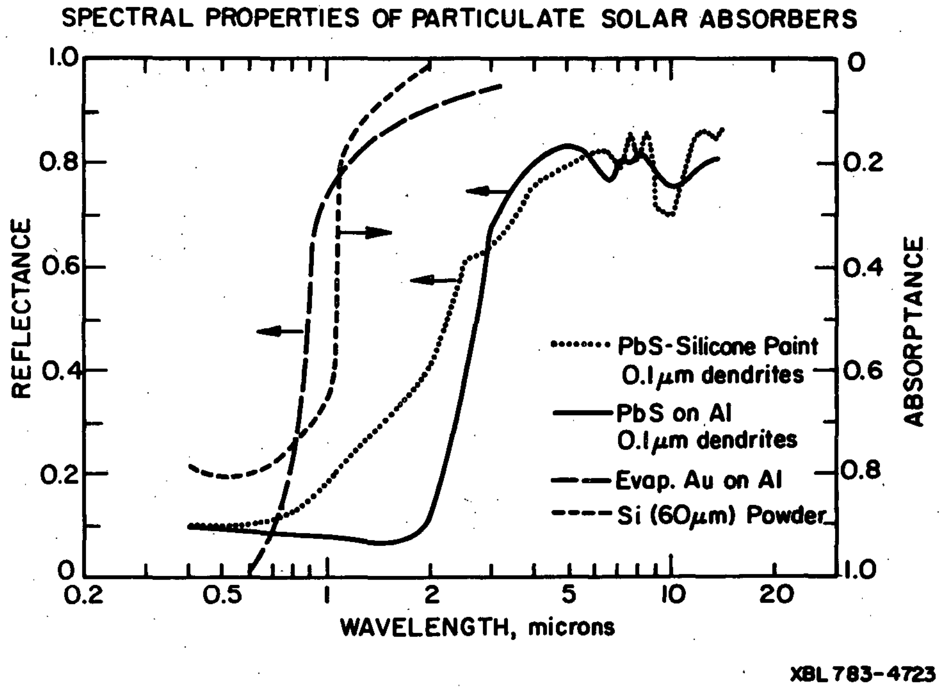

Fig. 11. Reflectance for particulate absorbers consisting of PbS, Williams et al. [19], evaporated gold on aluminum, Lee [23], and silicon powder coatings Warren [21].

a semiconductor metal tandem. However, the nature of surface scattering remains as a very important consideration when such systems are employed as solar absorbers.

One hope in the utilization of the particle scattering phenomena for solar energy collection is by use of very fine particle sizes. If a paint consisting of very fine pigment particles could be made to satisfy the requirements for the Maxwell-Garnett Theory, then a painted metal might make a good selective absorber. This technique has already been attempted with some success by Moore et al. [22].

3.4. Semiconductor/Metal Tandems

Metals naturally provide a high infrared reflectance, which is required of selective absorbers for suppression of thermal emittance losses. However, the solar absorptance for a metal is insufficient so that it alone would not be a practical absorber. To be a good absorber, the metallic layer must be covered by some type of solar absorbing layer. Semiconductors are fairly well suited for this application because many exhibit band related absorptions in the visible wavelengths and band transition in the infrared wavelengths. If a metal is overlayed with a semiconductor then the semiconductor will absorb high energy solar radiation, while in the infrared wavelengths the tandem will act like a poorly emitting metal. The metallic like character of the tandem is due to the high transparency of the semiconductor in this region. A schematic cross section of a tandem absorber is shown in Fig. 12.

One of the simplest single layer absorbers is an oxidized metal, where the oxide provides the necessary solar absorptance. Figure 13

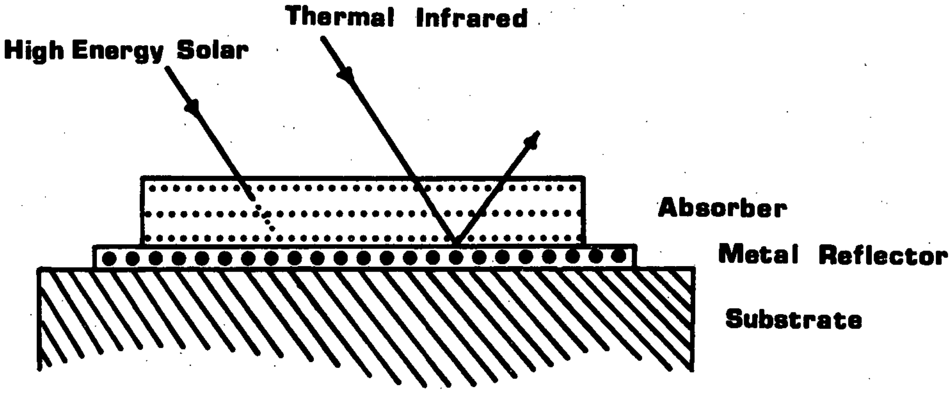

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Fig. 12. Schematic cross section of a semiconductor-metal tandem selective absorber.

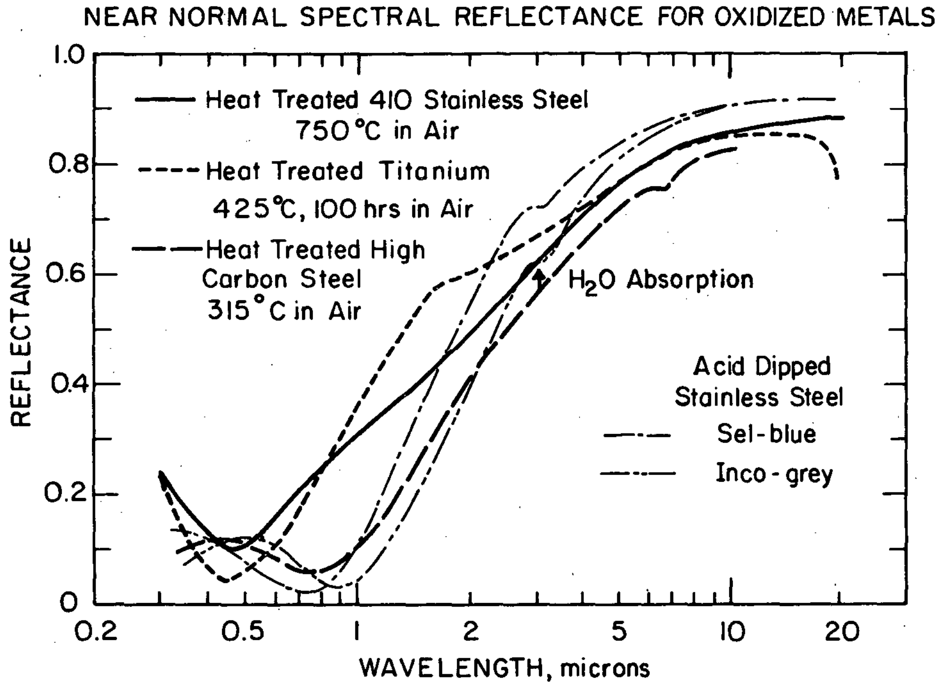

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Fig. 13. Reflectance of natural oxides found on stainless steel and titanium, Edwards et al. [24]. Acid treated stainless steels are shown for both INCO and SEL processes investigated by Karlsson and Ribbing [61]. A heat treated mild carbon steel is shown for comparison, Borzoni [74].

shows three representative oxides. Such natural oxides appear very promising, if they can be stabilized and made to exhibit similar mechanical properties seen in the substrate. With temperature cycling, oxides can crack or spill, which may be a major draw back in their usefulness. Recently a technique has been perfected to color stainless steel by hot acid dipping. As a result, a complex oxide coating is formed and can be used as a tandem absorber (see Fig. 13). This technique has been analyzed by Karlsson and Ribbing [61]. They found that if this coating was to be used above 200°C it would require a passivating layer.

There are numerous semiconductor-metal combinations; a number of successful types are shown in Fig. 14. The oldest and possibly the easiest to make is CuO on Al; it was formed by spraying a solution of CuO on the metal plate and heating to make the final absorber. The other copper oxide surface noted in this figure is formed by a chemical conversion process much like methods to be discussed later. The lead sulfide coating was vacuum evaporated over aluminum. This PbS coating shows an interesting contrast to that of the PbS dendrite particulate coatings. Cobalt oxide is a known refractory oxide and recent work has applied this coating to solar absorbers, by electrodeposition, oxidizing, and doping procedures.

Another interesting tandem absorber is that of In_2O_3 on silicon investigated by Goldner and Haskal [28]. This coating combination works in reverse of the regular tandem coating. The top layer reflects the infrared wavelengths while the bottom silicon layer absorbs the high energy visible light. In the visible range In_2O_3 appears transparent,

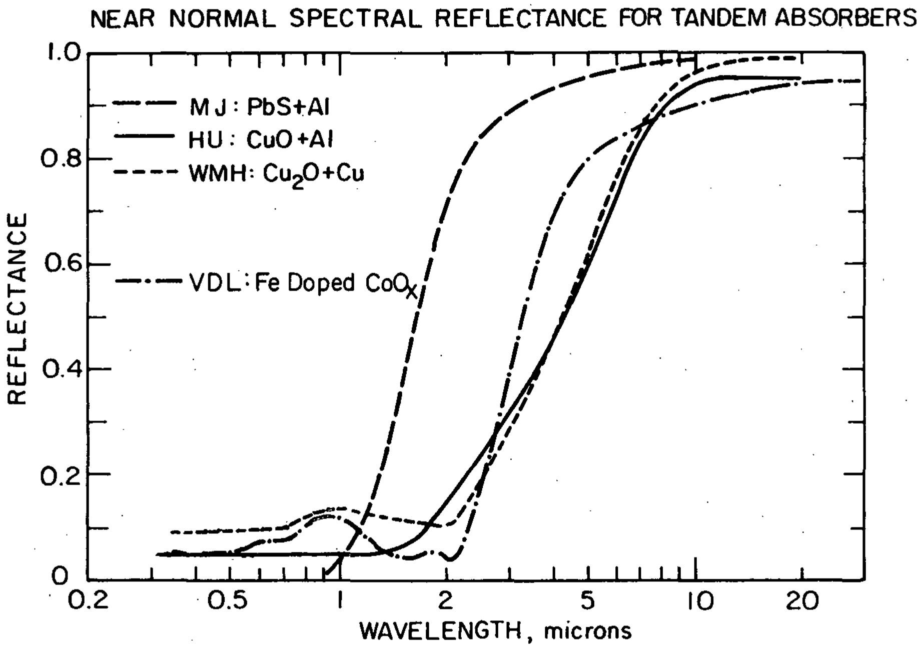

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Fig. 14. Reflectance of various tandem absorbers--lead sulfide on aluminum, MJ, McMahon and Jasperson [25], copper oxide on aluminum HU, Hottel and Unger [27], Cu_2O on copper, Watson-Munrd and Horwitz[26], and thermally converted Fe doped CoO_x, Van Der Leij [78].

as may be seen in the section on heat mirrors. The reflectance for this unusual absorber is shown in Fig. 15.

A well refined tandem absorber is the University of Arizona's silicon absorber, produced by Seraphin and co-workers [3], shown schematically in Fig. 16. It consists of a silver reflection film covered by a diffusion barrier (anti-agglomeration layer), in turn covered with a silicon absorber. To reduce the high reflectivity of the silicon layer an antireflection layer is used. This may seem to be an over designed absorber but it is one of very few surface coatings which can withstand continuous temperatures in excess of 500°C with good stability. The reflectance of this high temperature absorber is shown in Fig. 17.

Tandem absorbers can be made from crystalline or amorphous materials in the form of powders or continuous films. Sometimes the presence of grain boundaries, imperfections or lack of atomic order can be beneficial in deriving the desired absorber characteristics. These absorber layers can be formed by various electrochemical, reactive and depositive means. It is because of all these factors that the tandem absorber is one of the most popular absorber designs.

3.5. Multilayer Thin Films

Multilayer thin films known as interference stacks are dielectric, metal combinations which act like a selective filter for energy absorption. The desired effect of an interference stack is to trap energy between semi-transparent metal, dielectric and metal alternations. Particular wavelengths of solar energy are absorbed by multiple reflection in the dielectric-metal layers. Other wavelengths not corresponding

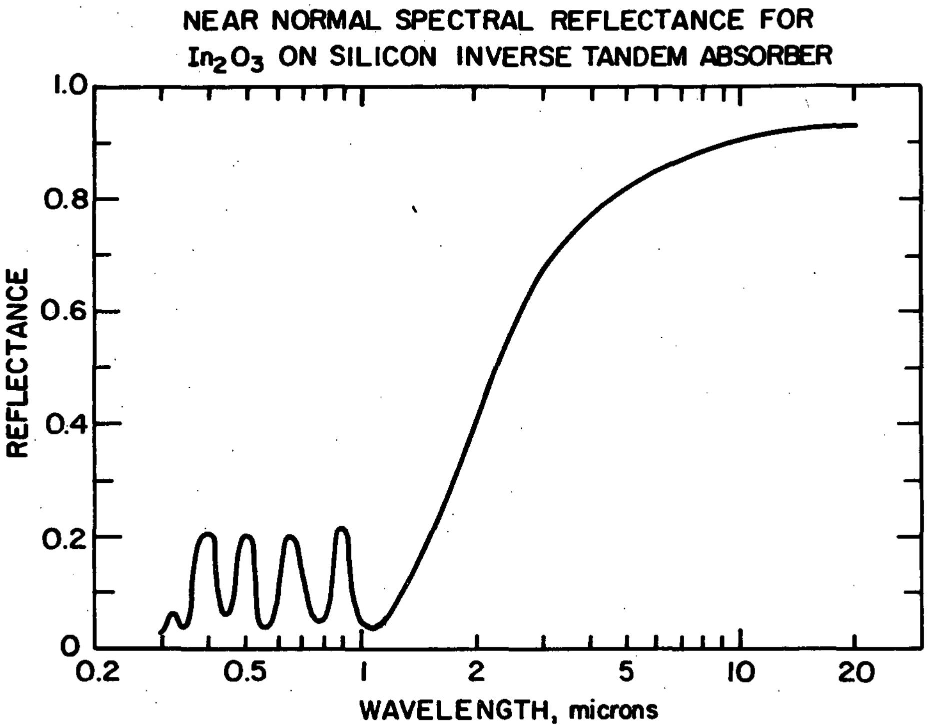

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Fig. 15. Reflectance for an inverse tandem absorber. The In_2O_3 layer acts like an infrared reflector while the buried silicon layer performs as a solar absorber, Goldner and Haskal [28].

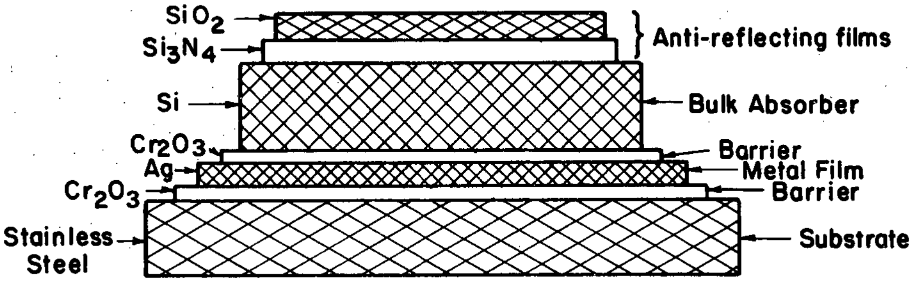

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Fig. 16. Cross section of a silicon photothermal absorber designed by the University of Arizona. This type can withstand temperatures in excess of 500°C, Masterson and Yoder [29].

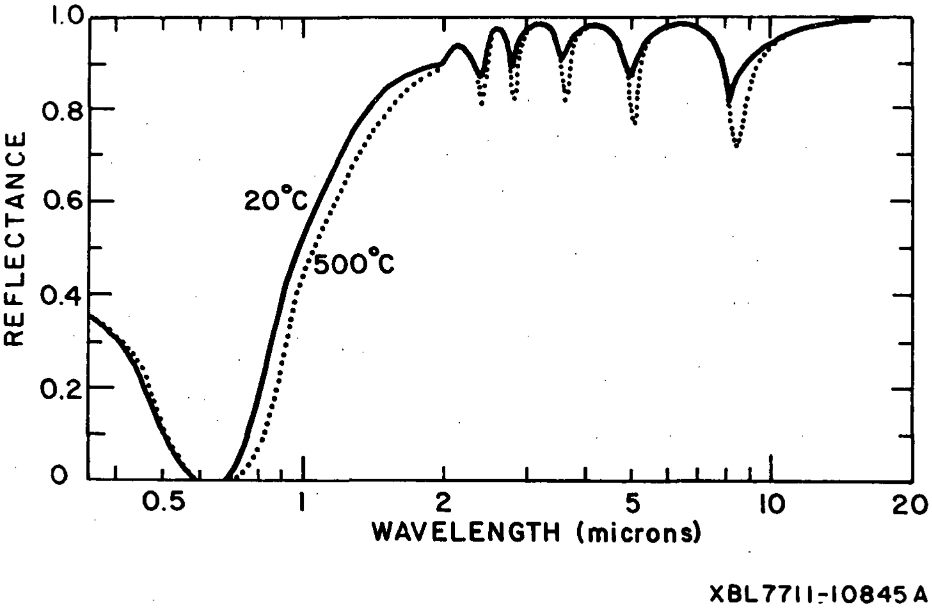
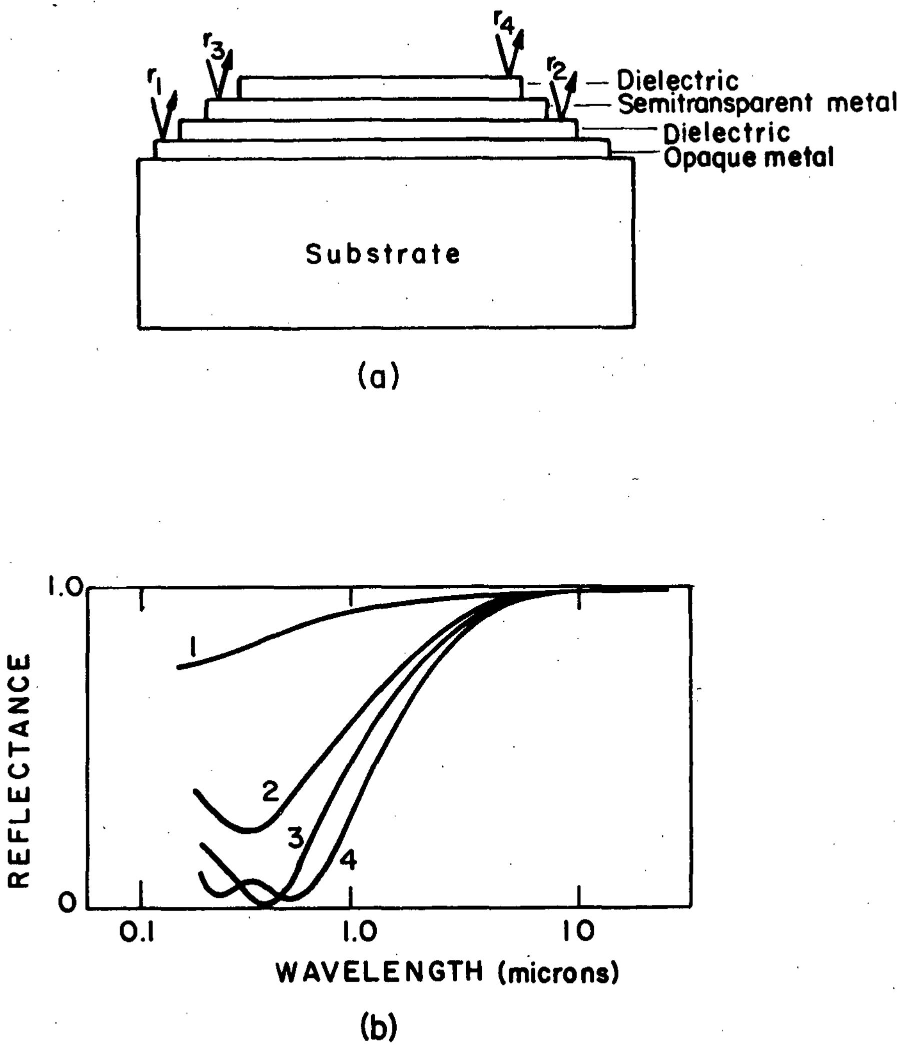


Fig. 17. Near normal reflectance of a silicon photothermal absorber, designed by the University of Arizona, Masterson and Yoder [29].

to the absorption frequency of these layers are reflected. For solar energy absorption, a broad band absorber is needed, as opposed to an optics application when only a single or narrow band of wavelengths might be altered by the absorption, transmission or reflection properties of thin films. The basic concept of a four layer film is shown in Fig. 18a. The second portion of this figure (Fig. 18b) is the optical response in terms of reflectance for the addition of each individual layer to the absorber. The layer marked (1) represents the reflectance for a metal. The next layer (2) corresponds to the dielectric of L/4 thickness, where L is the desired absorbed wavelength. In general the dielectric need not exhibit intrinsic absorption in the visible energies. On top of the dielectric is placed a thin metal, usually ~50Å thick, to appear semi-transparent to incoming radiation. Being such a thin layer the actual composition is not well defined. Most of the incoming energy in believed to be attenuated in this metal layer. Quantum size effects, to be discussed layer, may help describe the actual process of absorption response. Most multilayer films are produced by vacuum deposition or chemical vapor deposition.

An example of a variation of the standard interference stack is electrodeposited black nickel; two examples are shown in Fig. 19. The Tabor coating exhibits the classic double minimum for interference films, shown around 0.4 and 1.0 micron wavelength. This coating consists of two layers ZnS and NiS brought about by a simple change in plating current density during electrodeposition. Honeywell has improved this process to give the upper curve in Fig. 19. Also by heat treating



XBL 7711-10815B

Fig. 18. (a) Schematic cross section of a four layer interference absorber consisting of two quarter wavelength dielectric layers separated by metal reflective layers. (b) Variation of reflectance response (r) with the addition of each successive layer (after A. B. Meinel).

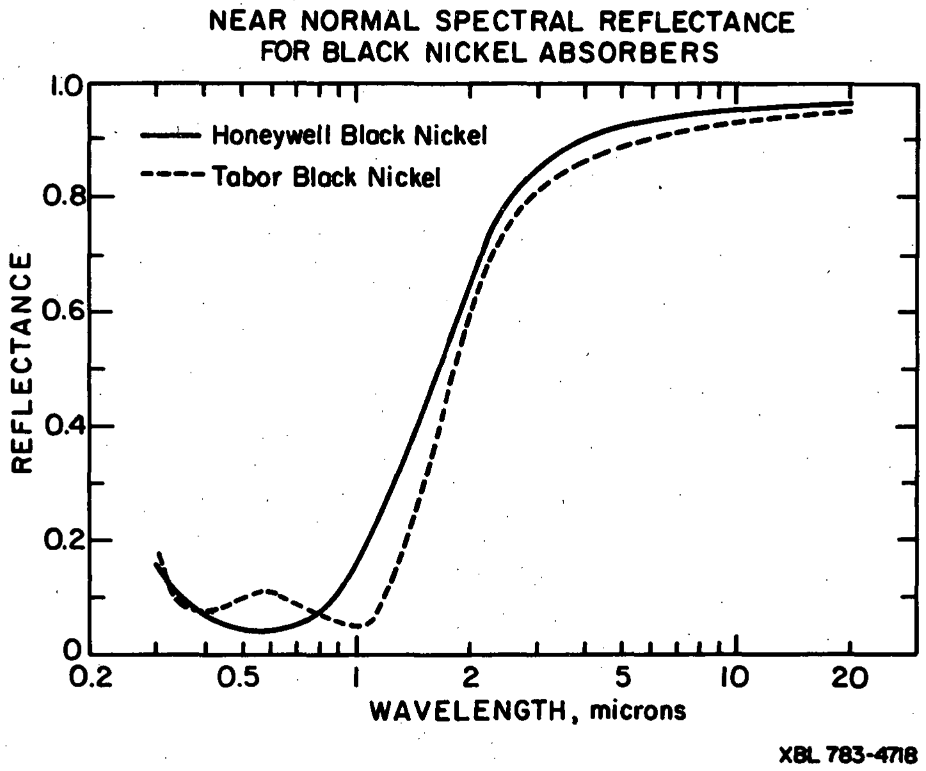


Fig. 19. Spectral reflectance for two types of black nickel. The recent coating is the Honeywell (Mar et al. [54]) type after being developed by Tabor [55].

the coating, drastic shifts in the optical transition wavelength can be made.

Other examples of multilayer coatings are shown in Figs. 20 and 21. The Helio 09 absorber reported by Meinel, et al. [30] exhibits a rapid rise in reflectance, but a bit too early in the spectrum to be a good absorber. A better response is obtained from the Helio 96 coating; which has a steep transition with good absorption. The last coating in Fig. 20 is the high temperature AMA coating (Al_2O_3 - Mo - Al_2O_3) developed for space use by Honeywell, investigated by Peterson and Ramsey [31] This coating can withstand temperatures in excess of 800°C while exhibiting good stability. In Fig. 21 an aluminum-SiO_2 made by Drummeter and Hass [32] absorber is shown. Note that this absorber shows the classic double minimum.

The disadvantage with most multilayer coatings is that they are fairly expensive to fabricate. Also, they can suffer from corrosion and interdiffusion at elevated temperatures. Each of these conditions result in degradation of the optical properties. Some coatings are sensitive to abrasion. The AMA absorber, on the other hand, appears not to suffer from many of these drawbacks. Some manufacturers of optical coatings claim that by use of automatic equipment and with high volume production, these vacuum deposited absorbers might be inexpensive.

3.6. Quantum Size Effects (QSE)

Quantum size effects occur in ultrathin films. These effects can result in the high absorption of visible light while maintaining a low infrared emittance. The critical thickness for the quantum

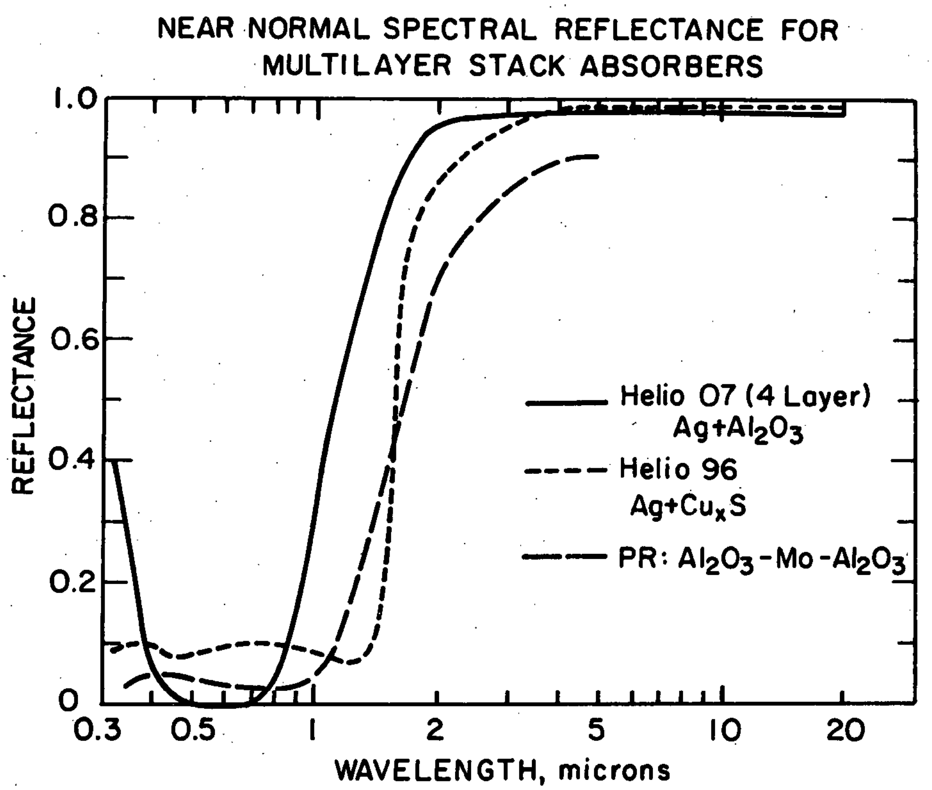


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Fig. 20. Reflectance for 3 types of multilayer absorbers. Two Heilo types, Meinel et al. [30], are shown for comparison to the Honeywell high temperature absorber, PR, Peterson and Ramsey [31].

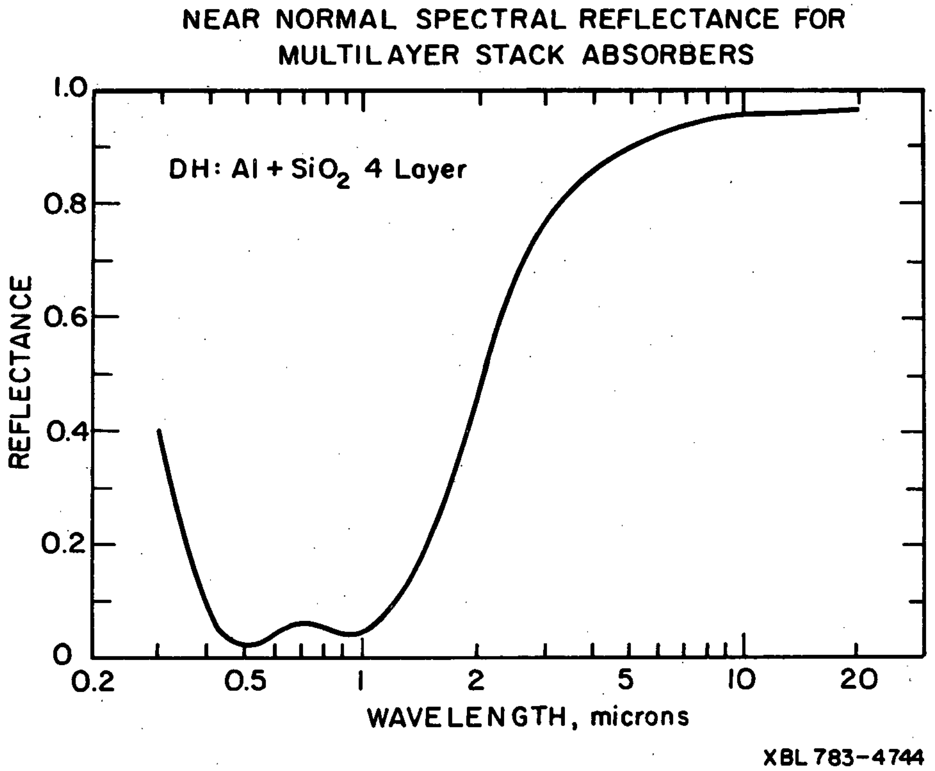

Fig. 21. Reflectance for a classic four layer absorber of SiO_2 on aluminum, Drummeter and Hass [32].

size effect to be utilized in a metal must be nearly the size 20-30Å and for a degenerate semiconductor, 100-500Å is necessary. The combination of a QSE material and a metallic substrate can make a selective absorber. This effect has been observed in vacuum deposited indium antimonide (InSb) on silver and aluminum substrates. The absorption coefficient was measured for this film and the results are depicted in Fig. 22 for various film thicknesses analyzed by Mancini and coworkers (see Ref. [33]). Similar results should be observed in semiconductors exhibiting sharp conduction band minima. This would require to exhibit a low value of the ratio of electron effective mass to that of its free mass in the thin film.

The QSE may play an important role in multilayer selective absorbers. Frequently, thin metallic layers are used between dielectric layers. These layers are responsible for high solar energy absorption; QSE may help explain this.

The major drawback in utilizing this effect in in a realistic solar absorber is the stability and continuity of composition of the coating upon cyclic heating and atmospheric exposure. To understand and utilize the quantum size effect, further work must be performed on various semiconductors and metals.

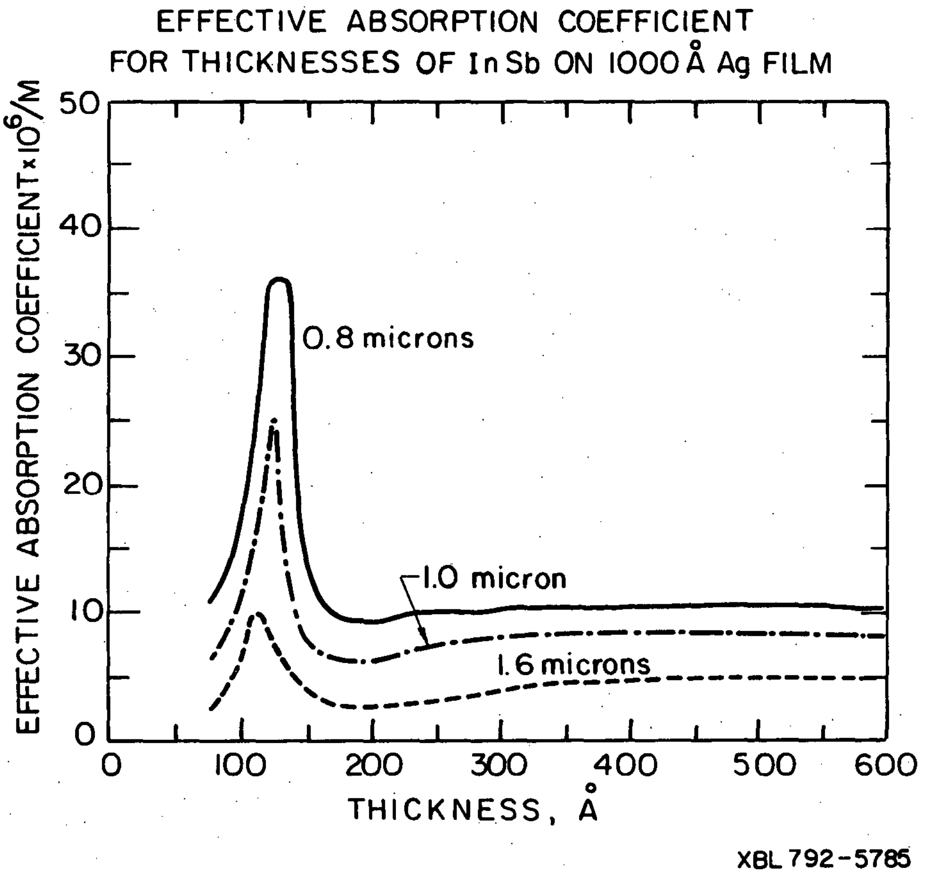

Fig. 22. The effective absorption coefficient for various thicknesses of InSb on 1000Å of silver, for various values of incident radiation Burrafato, et al. [33].

Table 2. Summary table of selective surfaces. The following table is as compiled for selected solar absorber coatings. All temperatures are °C, listed in parenthesis.

Material	Fabrication Technique	a	e (Low T)	e (High T)	Stability °C	Ref.
Ge	Gas evap.	0.91	0.2(160)	0.5(350)		34
Ge	Vac. evap.	0.61	0.54(240)	0.54(240)		34
Ge	Paint (Silicon binder)	0.91	0.8(200)			34
Si (on Ag)	CVD + AR Coating	0.80	0.05(100)	0.07(500)	500(v)	8
Si	Paint	0.83	0.7(200)			34
HfC	Intrinsic	0.65	0.1(100)			3
Al	Anodized, $KMNO_4$	0.80	0.35(<100)			34
Ni	Dendrites	0.95	0.3(100)- 0.6(100)			85
PbS	Vac. deposit	0.98	0.2(240)	0.3(300)	300	34
PbS	Paint (Silicon binder)	0.94	0.8(200)			34
PbS	Paint	0.90	0.4(100)			19
Cu_2S	Chem. Conv.	0.79	0.2(200)			34*
$Cu+CrO_x$	Paint	0.92	0.30(100)			8
N_iS-ZnS	Electrodeposit	0.88	0.1(100)	0.16(300)	<220	34[‡]
	" 2 layer	0.96	0.07(100)		<280	29[‡]
	" 3 layer	0.91	0.14			57[‡]
WC + CO	Plasma spray	0.95(600)	0.28(200)	0.4(600)	>800	34
W	Dendrite	0.80	0.10(100)		500	7
W/WO_3	Dendrite	0.90	0.18		<223	59
CrO_x+Cr/Ni	Electroplate	0.95	0.07(<100)		350	37[§]
CrOx-Cr/Sn	Electroplate	0.97	0.06			77[§]
CrO_x-Cr	Electroplate	0.95	0.10(100)	0.2(350)		16[§]

Table 2. Continued.

Material	Fabrication Technique	a	e (Low T)	e (High T)	Stability ^{o}C	Ref.
Cr_2O_3+Cr	RF sputtered	0.92	0.08(121)		300	14
Cr_2O_3+Co	Plasma spray	0.90(800)		0.5(800)	800	34
CuO_x	Chem. Conv.	0.91	0.16(<100)	0.4(200)		34
PbO_2	Electrodeposit	0.98	-			75
Fe+Mn+CuO_x	Dip coated paint	0.92	0.13(100)		>150	56
CuO/Au	Paint	0.8	0.06		>600	56
CuO/Ag/ Rh_2O_3	Paint	0.9	0.1		<400	57
F doped SnO_2	Paint	0.92	0.14		200	56
Al_2O_3+Au	Sputtered	0.95	0.025(20)		<300	58
Al_2O_3+Cu	Sputtered	0.9	0.045(20)		<200	58
MgO+Au	RF Sputtered	0.93	0.1		<300	57
Al_2O_3+Ni	Vac. evaporation	0.94	0.16(100)	0.35(500)	500	56
Al_2O_3+Pt	Vac. evaporation	0.94	0.3(500)		600	57
Si+CaF_2	Sputtered	0.7	0.1			56
Ge+CaF_2	Sputtered					56
Al_2O_3/ ZrC_xN_y/Ag	React. sputtered	0.91	0.05		175(A) 700(v)	56
Maxorb	-	0.97	0.10		150	57
Solartex	Electrodeposit	0.95	0.16(310)		700	57
Solartox	Electrodeposit	0.92	0.20		200	57
Au-smoke	Gas Evaporation	0.99	0.1		100	57
Steel	Acid dip	0.91	0.1(100)		200	61

Table 2. Continued.

Material	Fabrication Technique	a	e (Low T)	e (High T)	Stability	Ref.
Al_2O_3/Ni	Co-evaporation composite	0.94	0.10(150)			65
Al_2O_3/Pt	Composite	0.94	0.07(150)			65
Mo/Si_3N_4	CVD	0.82	0.08			68**
Mo/α-Si	CVD	0.77	0.10 est.			68
CoO_x	Anodized electro-deposit	0.93	0.24(260)			71
$(Cr$-Ni-$Va)O_x$	Electrodeposit	0.94	0.40(260)			71
Alcoa 655	Conversion coating for Al.	0.93	0.35		>163	72
Electro-black	Electrodeposit	0.86	0.05			73
CoO_x	Electrodeposit & heat treat	0.87 (AM2)	0.07(60)			78[+]
Fe_3O_4	Conversion coating for steel.	0.83 (AM2)	0.06(60)			78
ZnO	Anodized zinc	0.95 (AM2)	0.08(60)			78
WO_3	RF sputtered on Ni	0.83 (AM2)	0.07(60)			78
Black Nickel	Electrodeposition on zinc	0.94	0.09(100)		<200	79
FeC_x	DC reaction sputtered	0.80	0.02(100)		<350	80
CuO	Selective etching of Al/Cu & baking	0.93	0.11			82*
Yazaki Buhin Co.	Conversion coating for stainless steel	0.93 (AM2)	0.11			81

Table 2. Continued.

Material	Fabrication Technique	a	e (Low T)	e (High T)	Stability °C	Ref.
CuO_x	Chem. spray	0.93	0.11(80)			34†
Co_3O_4	Thermal oxide	0.90	0.3(140)		>1000	34
340 stainless steel	Chem. Conv.	0.91				34
	Thermal oxide	0.82	0.15(100)			34
Steel (F_3O_4)	Chem. Conv.	0.90	0.07(90)	0.35(200)		34
In_2O_3+Si	Vac. evap.	0.85	0.07			28
<u>Multilayer Films</u>						
Al/Ge/SiO	Vac. evap.	0.79	0.012(100)			60
Al/PbS/SiO	Vac. evap.	0.89	0.018(100)			60
Ni/Ge/SiO	Vac. evap.	0.88	0.035(100)			60
Ni/PbS/SiO	Vac. evap.	0.93	0.043(100)		240(A)	60
Cr/Ge/SiO	Vac. evap.	0.93	0.11(100)		240(A)	60
Cr/PbS/SiO	Vac. evap.	0.94	0.12(100)		240(A)	60
SiO/Cr/SiO	Vac. evap.	0.88	0.1		<450	34
Al_2O_3/Mo/ Al_2O_3	Vac. evap.	0.85–0.95	0.34(100)	0.11(500)	550	36
MgF_2/Sn (part.)	Vac. evap.	0.95	0.01			2
Ag/Al_2O_3	Vac. evap.	0.70–0.75	0.1			30
Ag/Cu_xS	Vac. evap.	0.90	0.1			30
OCLI	Vac. evap.	0.95	0.05(100)		300	35

Table 2. Continued.

Material	Fabrication Technique	a	e (Low T)	e (High T)	Stability °C	Ref.

Price estimates of a few commercial coatings are as follows:

OCLI	$38/m^2 (>930 m^2), $16/m^2 (>9300 m^2) est.	(35)	
Black Chrome (CrO_x)	$7.50-$8.60/m^2	(38)	
Black Copper (CuO_x)	$5.40/m^2	(38)	
Black Zinc	$7.50-$8.60/m^2	(38)	
Black Chrome (CrOx) + Ni layer	$15.80-$11.80/m^2	(>223 m^2)	(Olympic plating, Canton, Ohio)

Several of these coatings are also known as: *Black copper; †Black cobalt, §Black chrome, ‡Black nickel, **Black moly.

4. NON-SELECTIVE AND MODERATELY SELECTIVE COATINGS

This group of solar coatings certainly is the easiest to apply and probably the least expensive of all the collector coatings. The non-selective black coatings consist of painted coatings, chemical conversion finishes or even electropolated surfaces, although some of the following coatings are classified as selective surfaces under specific manufacturing conditions.

There are many types of painted coatings. The list which follows this discussion will cover the properties of a few representative paint coatings. Ordinarily, high temperature and heat resistant black paints are used chiefly in industry as protective coatings for metals. In some cases specific colors are used for their heat control properties. Very few of these paints were formulated with solar energy collection in mind as this is an area of research just developing. Common pigments used to manufacture black paint are carbon black (0.02-0.09 microns) iron oxide Fe_3O_4 (0.5 microns), amorphous graphite, bone black (325 mesh) and asphalt bases noted by Bolz and Tuve [5].

Degradation properties in terms of solar spectral response (emittance, absorptance) with varying time or temperature, are little known. In many cases the spectral responses indicated should be viewed with caution, for they may represent somewhat ideal conditions and accuracy is uncertain. When typical paints are applied to collector surfaces they will exhibit spectral responses quite different from that of the controlled thickness coatings applied to carefully polished metal surfaces.

Depicted in Fig. 23 are reflectance curves for fairly common black paints. Most of these are available as spray paints and do not require curing by baking, although certain types of 3M Black Velvet require it. Both Sherwin-Williams and Krylon paints can withstand about 100°C operating temperatures, while the 3M paint withstands 150°C. It must be noted that the temperature ratings of all paints reviewed are mechanical adhesion ratings and are not to be viewed in terms of optical degradation; that is, optical degradation may take place at even lower temperatures. The infrared absorptions noted in Fig. 23 are due to inherent absorptions in the paint binder. Higher temperature paints are shown in Fig. 24. The Cal Custom paint is a coating consisting of iron oxide pigment in a silicon binder; the absorption in the infrared is caused by this binder. The Parsons paints are lower temperature paints shown for comparison. The Cr_2O_3 paint has a dense black stain added to a normally green pigmented paint. This particular paint shows some selectivity. Various painted coatings in terms of their operating temperatures and characteristics are shown in Table 3. This tabulation is meant only to represent potential coatings and the actual feasibility of a particular coating for a solar application is still unknown in most cases.

Chemical conversion coatings exhibit the potential for low cost collector coatings and some coatings tabulated in Table 4 show moderate solar selectivity. Chemical conversion consists of dipping a metallic surface into a strong oxidizer or sulfidizer which subsequently forms an oxide or sulfide coating on the metallic base. Usually, this surface is integral with the base metal, which is different from a painted

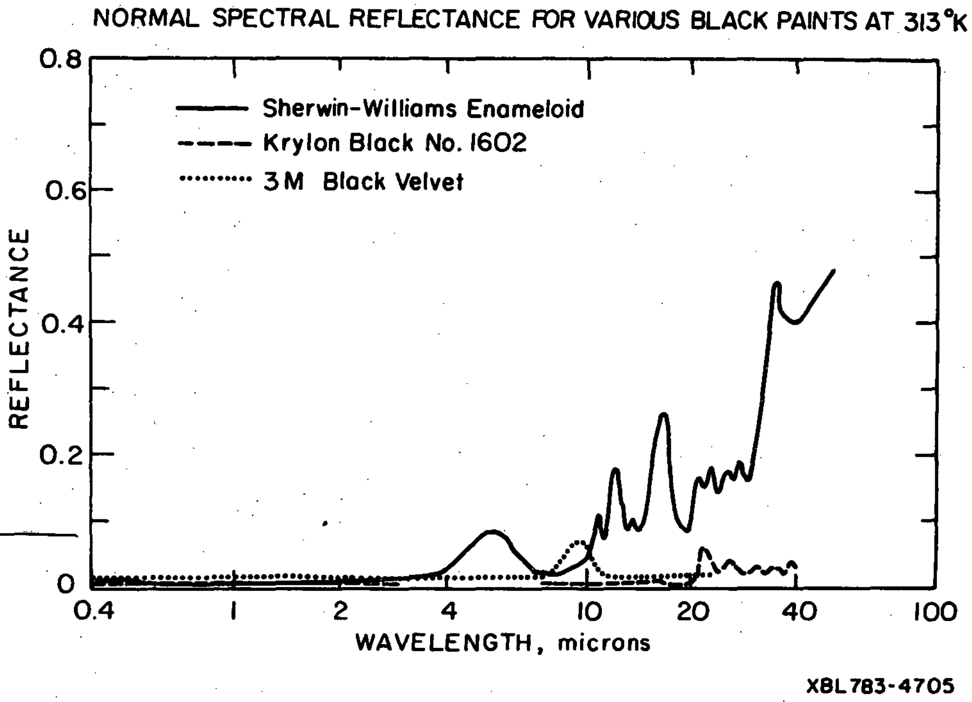

Fig. 23. Normal spectral reflectance for various black paints Touloukian [6], measured at 40°C. Presented in order are Sherwin Williams Enameloid Flat Black on aluminum substrate. Krylon Black No. 1602 on aluminum substrate. 3M Nextel Black Velvet on aluminum, e = 0.93, Hogg and Smith [13].

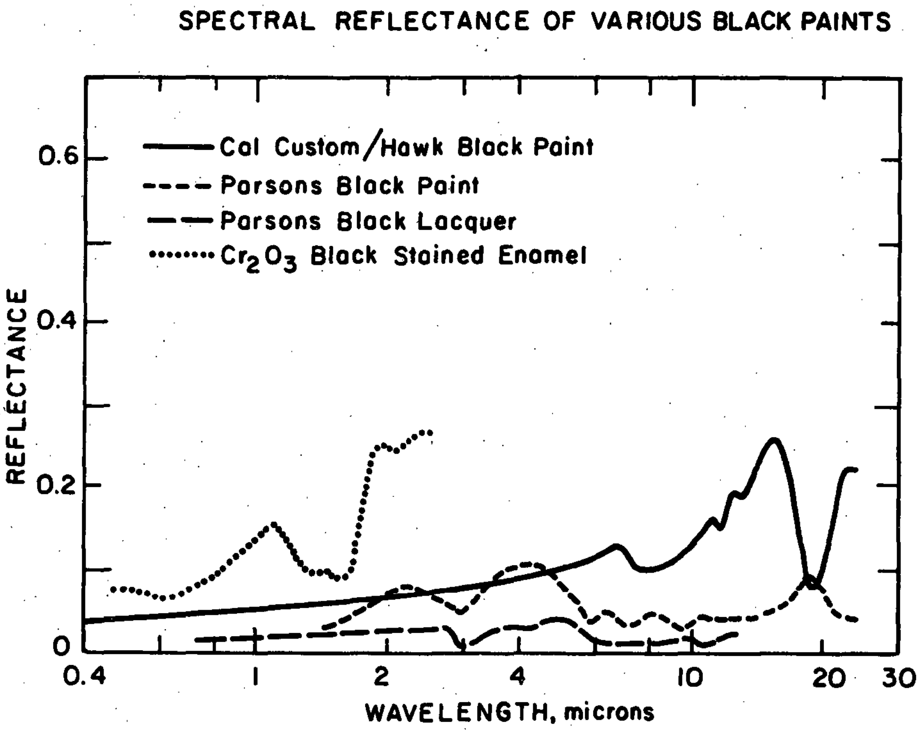

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Fig. 24. Hemispherical spectral reflectance at 30°C for Cal Custom/Hawk heat resistant coating on galvanized steel, Fan and Sprua [14]. Near normal spectral reflectance for Parsons' black paint on copper and black lacquer on brass and Cr_2O_3 pigmented (black stained) paint using NBS frit number 332, all at 25°C.

Table 3. Black paint coatings. All data taken from manufacturers' product literature, accuracy or completeness has not been verified.

Manufacturer and Trade Name	Highest Operating Temp.	Type	Notes
Tempil (So. Plainfield, NJ)			spray & bake
Pyromark Series 2500	1371°C	iron oxide + silicone	Refractory coating a=0.95 e=0.80 (315°C) e=0.95 (871°C)
Pyromark 800	427°C	silicone polyester	
3 M (St. Paul, MN) Nextel Black Velvet (101,110,401)	149°C	carbon black + silicon dioxide	a=0.97-0.98 (22°C) (25°C) gloss=0 (16°C)
Mobil 37-J-4 (Azusa, CA	204°C	gilsonite + oil	Heat, and moisture resisting black
Cal Custom/Hawk (Carson, CA)			
Heat Proof Coating #8029 (50-41)	649°C	iron oxide + modified silicone	Spray & bake coating
Sherwin Williams Stack Paint B68	260°C	---	
Cr_2O_3 Black Enamel	800°C	Cr_2O_3 + ceramic frit	e = 0.7 (480°C-800°C)

Table 3. Continued.

Manufacturer and Trade Name	Highest Operating Temp.	Type	Notes
Parsons Black Paint	130°C	---	a = 0.98 (25°C) e = 0.90 (130°C)
Sperex (Gardena, CA) VHT Flameproof coating SP 102	650°C cont. up to 815°C	Inorganic pigment & modified silicone	Spray & bake e = 0.82
Maas & Wahlstein Co. (Newark, NJ) Syncryl Enamel	232°C	Pigment + acrylic base	Brush or spray & bake (73 mm film thickness) can be textured.
Durachem	177°C	Epoxy base	Brush & spray & bake. Good chemical resistance & weathering.
Gavlon Ind. (Austin Texas) 719 Heat Resistant	204°C	Silicone acrylic base	Spray designed for steel
Ergenics (Waldwick, NJ) Novamet 150 Black Coating	815°C	Inorganic Pigment + alkaline water base	Brush or spray no baking
Ball Chemical (Glenshaw, PA) G-3858 High Temp. Black	315°C	--	Gloss=60+% semi gloss
G-313 High Temp. Black	649°C	--	Must be cured
Dampney (Everett, MA) Thurmalox 270 Series	537°C (resists 615°C)	Silicone base	Brush or spray, heat cured 19-26 m thick

Table 3. Continued.

Manufacturer and Trade Name	Highest Operating Temp.	Type	Notes
Rust-Oleum (Vernon Hills, IL) 412 Flat Black	121°C withstands 177°C	carbon black + oil-alkyd base	gloss=0-5%
4279 Heat Resistant Flat Black	427°C	Carbon black + silicone-alkyd base	gloss=5-15%
5779 Midnight Black	177°C	Carbon black + acrylic emulsion.	gloss=40-60% water reducible semi gloss

Table 4. Selected black conversion coatings. All data is taken from manufacturer's product literature, accuracy or completeness has not been verified.

Manufacturer and Trade Name	Type	Temp. & Time	Deposit Characteristics
Enthone: (West Haven, CT) Ebonol S-34	Caustic Oxidizer for Steel	140°C at 3-25 min	$Fe(FeO_2)_2$ 1-5 μm thick
Ebonol C	Caustic Oxidizer for Copper	100°C at 5-10 min	CuO (1.3-5 μm thick) Stable to 204°C
Ebonol Z-80	Mild Alkalizer for Zinc	38°C at 3-10 min	Metal oxide (1-2.5 μm thick) Stable to 170°C
Ebonol SS-48	Oxodizer Stainless Steel	127°C at 5-15 min	Oxide/sulfide 1.5-2.5μm thick
Enthox ZB-992	Acidic Strong Oxidizer	21-32°C at 0.5-3 min	Chromate Conversion
Conversional Chemical Corp. (Rockville, CT)			
Kenvert ZB	Oxidizer for Zinc	88°C at 1-2 min	
Kenvert 311	Oxidizer for Zinc	29°C at 20-30 sec	
Birchwood Casey (Eden Prairie, MN)			
Presto Black	Non-Caustic Solution for ferrous metals	15-20°C at 60 sec	Can be applied by hand
Aluma Black	Cold Conversion for Aluminum Non-Caustic	15-20°C at 1-2 min	Can be applied by hand

Table 4. Continued.

Manufacturer and Trade Name	Type	Temp. & Time	Deposit Characteristics
Antique Black	Cold conversion for copper		
Zinc Black	Cold conversion for zinc		
Allied-Kelite: (Des Plaines, IL)			
Key Kote 70 Blackening Agent	Zinc Phosphate for Ferrous metals	21-38°C at 0.5-4 min	
Du-Lite Chemicals (Middletown, CT)			
Du-Lite Black	Chemical Finish for Steel	149°C at 5-15 min	
Du-Lite 3-0	Chemical Finish for Stainless Steel	115°C at minutes	
Du-Lite Cu Black	Copper Oxidizer	100°C at minutes	
Heatbath Corp. (Spring Field, MA)			
Nickel Penetrate	Steel Alkaline Oxidizer with Nickel	143°C at minutes	Fe_3O_4 at 0.0001 in. operates up to 482°C
Enequist Corp. (Brooklyn, NY)			
Ultrex Z-27	Acidic Solution for Zinc	30-49°C at 1-5 min	
R.O. Hull Co. (Cleveland, OH)		54-82°C at 3-8 min	Mild corrosion protection

Table 4. Continued.

Manufacturer and Trade Name	Type	Temp. & Time	Deposit Characteristics
Roblack Zn-72	(0.002 in. + thickness		
Roblack Zn	Mild acid oxidizer for zinc	21-66°C at 1-5 min	Mild corrosion protection
Roblack Fe	Strong alkali oxidizer for steel	138-149°C (boiling)	iron oxide 0.25 μm
Roblack Cu	Strong alkali oxidizer for copper	99-103°C at 5-15 min	copper oxide, corrosion resistant, etching needs for dull surface
IRCO Blackjack 53000	Acid conversion finish for steel	27-38°C at 0.25-1.5 min	matte black
Mitchell-Bradford (Milford, Conn.)		77-82°C	
Electroless	Alkaline oxidizer for		
Black Magic	aluminum	0.5-10 min	
Turco Products			
Ferrotone	dizer for steel	150°C	

Table 4. Continued.

Manufacturer and Trade Name	Type	Temp. & Time	Deposit Characteristics
A. F. Holden Co. (Milford, MI)			
Permablack	For Ferrous Metals	115-121°C at 5-15 min	Black Oxide
Lustre Black	For Ferrous Metals	140°C at 15-30 min	Iron Oxide Film

NOTE: Strongly alkaline materials and oxidizing agents are harmful to operators; proper safety procedures must be followed. Also, liquid and dry oxidizer can constitute an extreme fire or explosion hazard around organic material or reducing agents.

or electrodeposited surface. The mechanical properties of the surface can be quite different from those of the substrate, though. Drawbacks with most of the conversion coating baths are both temperature and safety. Many processes are run at 100-150°C and are very corrosive. The Birchwood Casey coatings, on the other hand, are safe enough to apply by hand at room temperature. Also, most conversion coatings for zinc operate near room temperature. Zinc conversion may be in question since zinc is known to form a white corrosion product readily, according to Poll [40]. The advantages of Chemical conversion are numerous: the coating is easily formed in a matter of minutes, the process is potentially inexpensive and there many kinds of coatings available for steel (including stainless), copper and aluminum.

In Table 5 a summary of potential non-selective and moderately selective coatings is shown. Only coatings with published a,e values are presented in the table.

Overall, both painted and chemical conversion coatings are very attractive because so many potential processes exist, they are fairly easy and inexpensive to apply. The equipment to apply these coatings already exists and the coatings are currently used for many commercial items. These coatings do have a potential to be selective absorbers. The painted coatings need a binder which is highly transparent or poorly emitting in the infrared wavelengths. The binder should not suffer from infrared absorptions and must withstand fairly high temperatures (at least 150-200°C). The conversion coatings need to be optimized and formed in such a way that they exhibit poor infrared emittance.

Table 5. Summary of non-selective and moderately selective paint and conversion coatings for solar collectors. Only coatings with published a and e values are listed in this table.

Manufacturer	Type	Absorptance/ Emittance	Characteristics
Ametek Inc.	Electroplated PbO_2 on copper	a = 0.98-0.99 e = 0.30	
Enthone	Copper immersion in hot alkali	a = 0.85-0.95 e = 0.10-0.40	Black oxide coating
Alcoa	Alkaline conversion	a = 0.93 e = 0.35	0.3-0.5 μm thick
Birchwood Casey	Acidic conversion for aluminum	a = 0.96-0.97 e = 0.55-0.73 (100°C)	
Permaloy Corp.	Anodized aluminum	a = 0.94 e = 0.71	5 μm thick
PyroMark	Iron oxide-silicone black paint	a = 0.80-0.95 (310-1100°)	
Cal Custom/ Hawk	Black iron oxide silicone paint	a = 0.95* e = 0.83 (20°C)	
Nextel	Carbon black + silicon dioxide	a = 0.96-0.98 e = 0.89 (25°C)	Withstands 150°C
Enersorb (De Soto, Inc.)	Black paint	a = 0.97 e = 0.92	
Solarsorb (Caldwell Chemicals)	Black paint C-1077	a = 0.9 e = 0.6-0.8	20 μm thick
Ferro Corp.	Black porcelain enamel	a = 0.97-0.98	Good durability
Novamet 150	Water base inorganic enamel	a = 0.96 e = 0.84(25°C)	Good stability

Table 5. Continued.

Manufacturer	Type	Absorptance/ Emittance	Characteristics
Rust-Oleum	Black Paints (3)	a = 0.95-0.96 e = 0.87-0.90	good durability
Rockwell S-31	Black Paint	a = 0.8-0.85 e = 0.8-0.85	stable above 550°C
Bostik 436-3-8	Black Paint	a = 0.90 e = 0.92	
C. H. Hare 7729	Black Paint	a = 0.96 e = 0.90-0.92	
Martin Marietta	Inorganic Paint	a = 0.9-0.95 e = 0.9-0.95	stable above 550°C
Exxon Black Paint	Silicone and Silicate	a = 0.98 e = 0.9	stable above 700°C
Ebonol C	Chemical Conversion-copper	a = 0.84 e = 0.06	
Ebonol S	Chemical Conversion-steel	a = 0.86 e = 0.07	
Ebonol Z	Chemical Conversion-zinc	a = 0.75 e = 0.13	
Black Magic	Conversion finishes for aluminum	a = 0.82 e = 0.12	
Climax Moly.	Dichromate conversion dip	a = 0.80 e = 0.6 0.02	425°C Bath for SS

All of these coatings need to be evaluated in terms of stability and lifetime with temperature cycling and the collector environment.

5. COLD MIRROR COATINGS

A basic cold mirror coating reflects the visible and ultraviolet radiation in the solar spectrum while becoming a poor reflector but good transmitter of infrared wavelengths. The transmittance and reflectance for an ideal cold mirror coating is shown in Fig. 25. Included in this figure is a commercial coating made by OCLI [42] for this particular purpose. This OCLI coating is a multilayer thin film broad band reflector produced by vacuum deposition. The multilayer film consists of a thin metal base overlayed with several thin dielectric layers. These types of coatings currently are being used for the separation of light and heat in film projectors and photo copiers. An interesting application for this coating is a combined thermal-photovoltaic system. In this hypothetical system high energy visible light could be separated from the lower energy infrared, unusable for photovoltaic generation but very useful for photothermal heating of fluids. The photovoltaic cell would also run cooler in the absence of the infrared energy. With such a system a more efficient and sensible use of the various energies of the solar spectrum would result.

Another application of cold mirror coatings is for greenhouses; greenhouses consume annually $36.9\text{x}10^{12}$ KJ of energy in the U. S., much of the form of natural gas according to Winegarner [43]. Plants use particular wavelengths of light in the visible region for photosynthesis. Plants only utilize wavelengths less than 0.75 microns, after Winegarner [44]. The remaining amount of energy in the solar spectrum is available as heat for the greenhouse. By use of cold mirror coating as shown in Fig. 26 and a baffle type greenhouse roof, photosynthetic energy

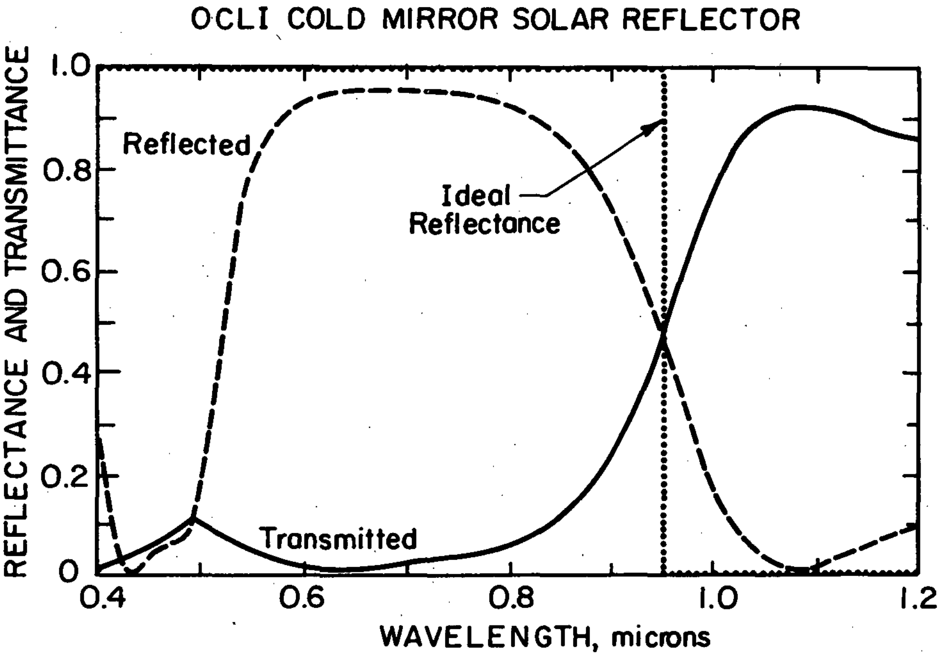

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Fig. 25. Spectral reflectance and transmittance for OCLI commercial cold mirror coating compared to the ideal mirror reflectance for a 0.95 μm transition wavelength, OCLI [42].

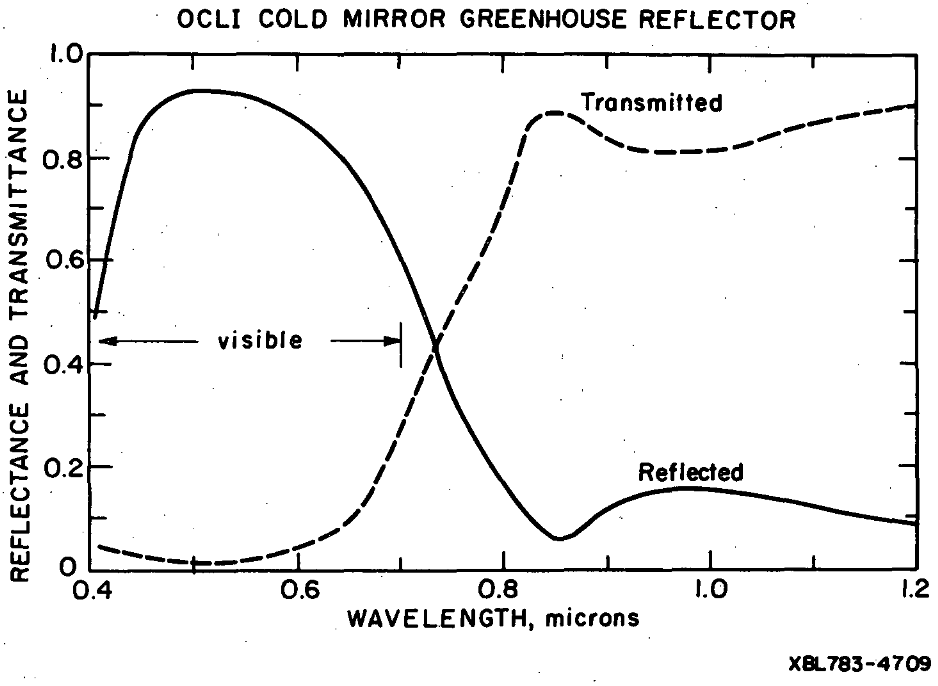

Fig. 26. Spectral reflectance and transmittance for OCLI greenhouse cold mirror coating, Winegarner [43].

can be reflected into the greenhouse while infrared energy is transmitted into air channels. Within these channels there would be air flowing across absorber surfaces. The resulting hot air could be used for heating of the greenhouse and rock storage system. In this way the crops receive the solar energy wavelengths needed for growth while allowing the grower to maintain fairly stable daily greenhouse temperatures by simple heat management of the storage systems.

6. HEAT MIRROR COATINGS

Heat mirror coatings are also called transmitting selective surfaces which consist of single or multilayer films. These films transmit the solar visible and ultra-violet wavelengths while exhibiting a high reflectance to infrared energy. The optical behavior of a heat mirror is directly opposite to that of a cold mirror. Heat mirror coatings fall into four categories: Semitransparent metal, conducting microgrids, Semiconductor single and multilayer types.

Heat mirror coatings can be made by a variety of methods. One rather simple technique consists of a spray and bake coating of fluorine doped stannic oxide (SnO_2). The more complicated tandem and multilayer films are deposited by sputtering and vacuum evaporation. Successful sputtered coatings include tin doped indium oxide (In_2O_3) single layer and $TiO_2/Ag/TiO_2$ multilayer films. Intrinsic materials such as doped indium oxide, doped stannic oxide (SnO_2) and lanthanum hexaboride (La_2B_6) exhibit a natural transmitting solar selectivity. However, this type of selectivity is not to be confused with that of a selective surface, which exhibits high visible absorption. Other types of popular coatings include the metal/oxide heat mirrors; these have been successfully applied to plastics and glass. The most promising tandem coatings are gold/titanium oxide on plastic and copper or silver/silicon dioxide for both glass and plastic abstrates.

In Table 6, a tabulation of pertinent optical properties of selected heat mirror coatings is shown for reference. Also in Figs. 27-28, the spectral transmittance-reflectance properties of heat mirrors are depicted, including several important commercial varieties. The major

Table 6. Optical Properties of heat mirror coatings.

Type	Effective Transmission (Vis)	Effective Emittance (IR)	Reference
OCLI Indium Multilayer	0.84 (0.85)	0.14	[46,44]
OCLI Silver Multilayer	0.72	0.17	[46]
MIT Sn doped In_2O_3 (RF Sputtered)	0.85 (AM2)	0.081 (121°C)	[45]
MIT 180Å T_iO_2/180Å Ag/180Å T_iO_2 (RF Sputtered)	0.54 (AM2)	0.071 (121°C)	[45]
MIT 330Å TiO_2/180Å Ag/180Å TiO_2 (RF sputtered)	0.67	0.065 (25°C)	[66]
0.35 μm Cd_2SnO_4/SiO_2 (sputtered)	0.78	~0.1 (150°C)	[65]
F doped SnO_2 (Solution baked)	0.75	0.70	[2]
		Reflectance (IR)	
MIT Sn doped In_2O_3 (microgrid)	0.9	0.83	[10]
5% SnO_2 doped In_2O_3 (aerosol pyrolysis)	0.90	0.85	[47]
L_2B_6	0.85	0.90	[48]
Sierracin, Intrex + AR			
Au/TiO_x/plastic (T42)	0.78	0.72	[67]
(Vac. Evap.) (T28)	0.80	0.87	[67]

Table 6. Continued.

Type	Effective Transmission (Vis)	Effective Emittance (IR)	Reference
Kinetic Coatings 51Å Cu/50Å SiO_2 (ion beam sputtering)	0.06(1) 0.16(2)	0.86(3)	[64]
78Å Cu/500Å SiO_2	0.11(1) 0.23(2)	0.90(3)	[64]
26Å Ag/500Å SiO_2	0.05(1) 0.14(2)	0.71(4)	[64]
41Å Ag/500Å SiO_2	0.14(1) 0.25(2)	0.84(3)	[64]

(1) Integrated with respect to AM2 Solar Spectrum (0.4-0.7 μm).

(2) Integrated with respect to AM2 Solar Spectrum (0.35-2.5 μm).

(3) Average reflectance (4-50 μm).

(4) Average reflectance (5-10 μm).

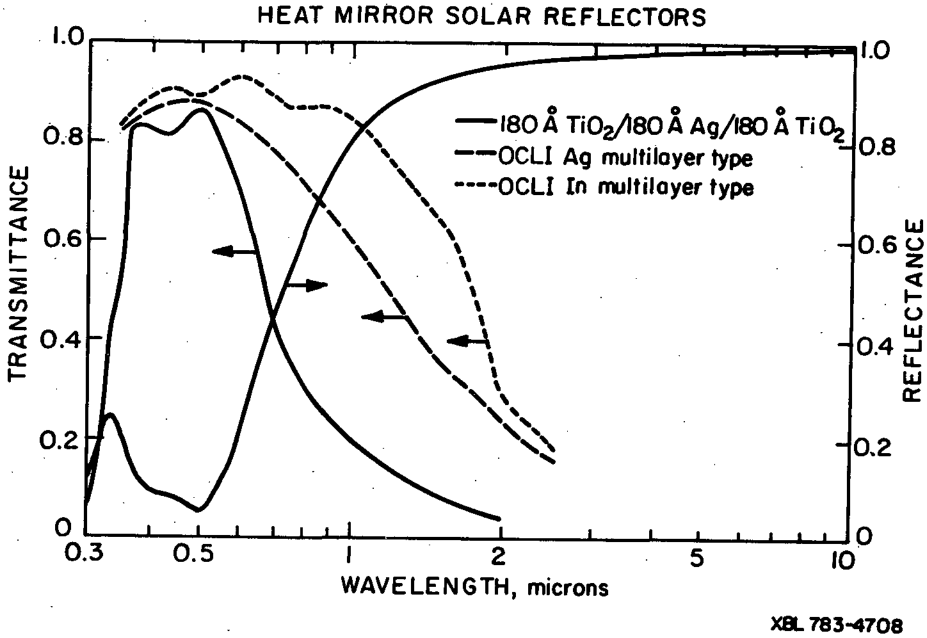

Fig. 27. Spectral transmittance and reflectance for various heat mirror coatings. The OCLI types are commercial coatings, Appel [46]. The TiO_2-Ag coating is an MIT experimental coating, Fan and Bechner [45].

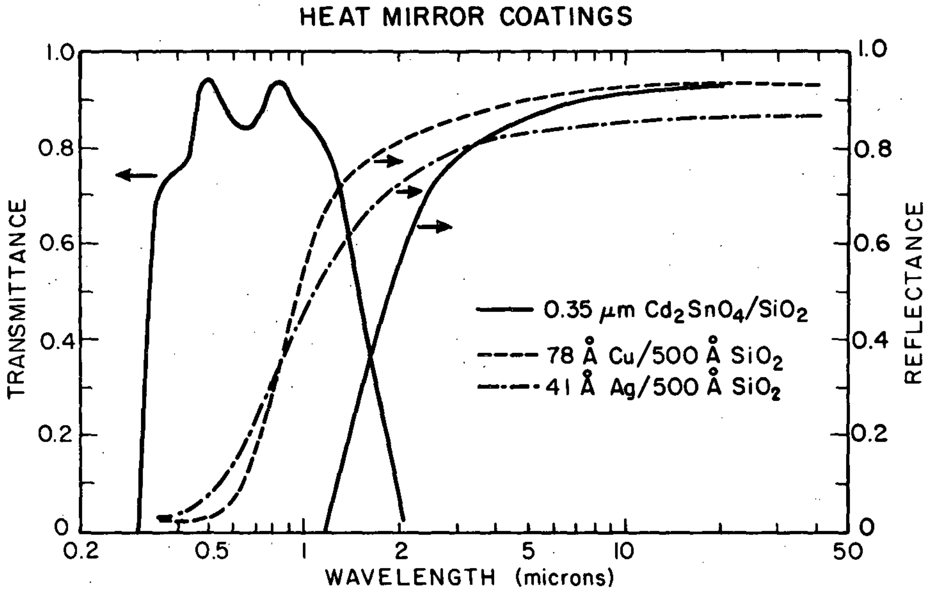

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Fig. 28. Spectral transmittance and reflectance for three heat mirror coatings. The experimental Cd_2SnO_4/SiO_2 coating was developed by Haake [65] of MIT. The metal/SiO_2 heat mirrors were by Kinetic Coatings, King [64].

application for these coatings is for a performance much like a selective surface if a heat mirror is used in conjunction with a standard black absorbing surface in a solar collector. In this application, the heat mirror coating is applied to the inside surface of a single glass cover collector or to the top surface of the inside cover of a double glass cover. This coating easily passes the high energy visible radiation with little absorption to the underlying black absorber. The absorber reradiates infrared energy at its operative temperature back to the cover. This energy is trapped by the heat mirror coating because of its high reflectivity in the infrared wavelengths. The net result is to absorb the visible energy and to poorly emit in the infrared, very much like a selective absorber. Heat mirror coatings have an advantage over selective absorbers in that they can operate at much lower temperatures.

An interesting question arises here--at high operating temperatures would the convection losses be so high that the selective surface would be favored over that of a heat mirror system? This leads to another application. It is known that with increasing temperatures, emittance of selective absorbers goes up. So if a heat mirror were used in conjunction with a selective surface at steam temperature in a concentrating collector, one would expect better efficiency from this system; it would remain to be seen whether this application would be cost effective in terms of energy gain. Still another question needs to be considered--when is it advantageous in terms of economics and efficiency to use evacuated collectors and should heat mirrors be used? All of these very interesting questions will be discussed in detail in a later section. A simple application for a heat mirror coating is control of temperatures in large office buildings, particularly when the building design requires a lot of glass. Heat mirror coatings can control the amount of heat allowed to come in or escape from the office environment while maintaining illumination levels.

An interesting heat mirror effect can be obtained by suspending a fine conducting mesh below the cover plate of a solar collector. A 0.25 μm mesh would behave like an electromagnetic filter. This mesh would appear as a transmitting material in the high energy visible while performing as an infrared reflector. Incorporating this mesh into a collector would mean that reradiated infrared energy from the absorber surface could be reflected back to it, thereby creating a drop in the net thermodynamic driving force for energy lost by the absorber, increasing collection efficiency.

7. ANTIREFLECTION COATINGS

Coatings can be used to control the surface reflections that occur every time electromagnetic radiation passes from one medium to another. For this discussion, the air-glass interface will be of primary importance, that is reflectance loss from collector covers. Antireflection films also are very important for the suppression of reflective losses associated with semiconductor surfaces such as with semiconductor-metal tandems and photovoltaics. For normal incidence, the fraction of light reflected from incidence is given by:

$$R = \left[\frac{n_0 - n_1}{n_0 + n_1}\right]^2$$

where n_0 and n_1 are the refractive indices of the medium the light is leaving (e.g., air) and of the medium the light is entering (e.g., glass). An air-glass cover plate transition exhibits $n_0 = 1.0$ and $n_1 = 1.5$, giving 4% normal reflectance per interface. An antireflection coating can reduce this loss by adding a quarter wavelength material of intermediate refractive index between air and glass. The effect of this coating is to cause destructive interference at the specified wavelength; nearby wavelengths are affected also by this film. If the refractive index of the coating material is n_2, the normal reflectance is now given as:

$$R = \left[\frac{n_0 n_1 - n_2^2}{n_0 n_1 + n_1^2}\right]^2 .$$

Reflection is zero if $n_2 = (n_0 n_1)^{1/2}$. The ideal coating for glass should have an index of refraction of 1.23, which is unfortunate because no suitable substance exists. A common optical coating is MgF_2 with n = 1.38. The spectral response of this coating, along with others, can be seen in Fig. 28. The MgF_2 coating reduces the reflectance to about 1.6% at 0.6 microns wavelength, which certainly is a significant improvement.

To get closer to the ideal coating, multilayer dielectric coatings are employed. Frequently, high index material is placed between the MgF_2 coating and glass to increase the effective index of glass; also, these layers can be used to broaden superior transmission properties over a wider spectrum. The use of intermediate coatings can be seen in Fig. 29 with the $MgF_2(n = 1.38)/CeO_2(n = 2.35)/CeF_2(n = 1.65)$ coating, studied by Meinel [2]. Also shown in this figure is one of OCLI's multilayer proprietary HEA coatings reported by Belber [49].

Another experimental material, where the purpose was to reduce reflective losses, is low index polymer coatings on glass. A coating of Teflon FEP dispersion (n = 1.34) appears to have promise according to Goldner and Haskal [28]. If Tedlar is used instead of glass, its transmittance can be increased by dipping in acetophenone.

Probably the least expensive treatment for glass is fluosilicic acid etch. This surface treatment, developed by Tomsen [51], primarily roughens by etching small pores, possibly in high calcium regions, leaving porous silica in the surface. This porous layer has cavities which are small with respect to the wavelength of light (200Å) giving this layer an effective refractive index less than that of solid glass,

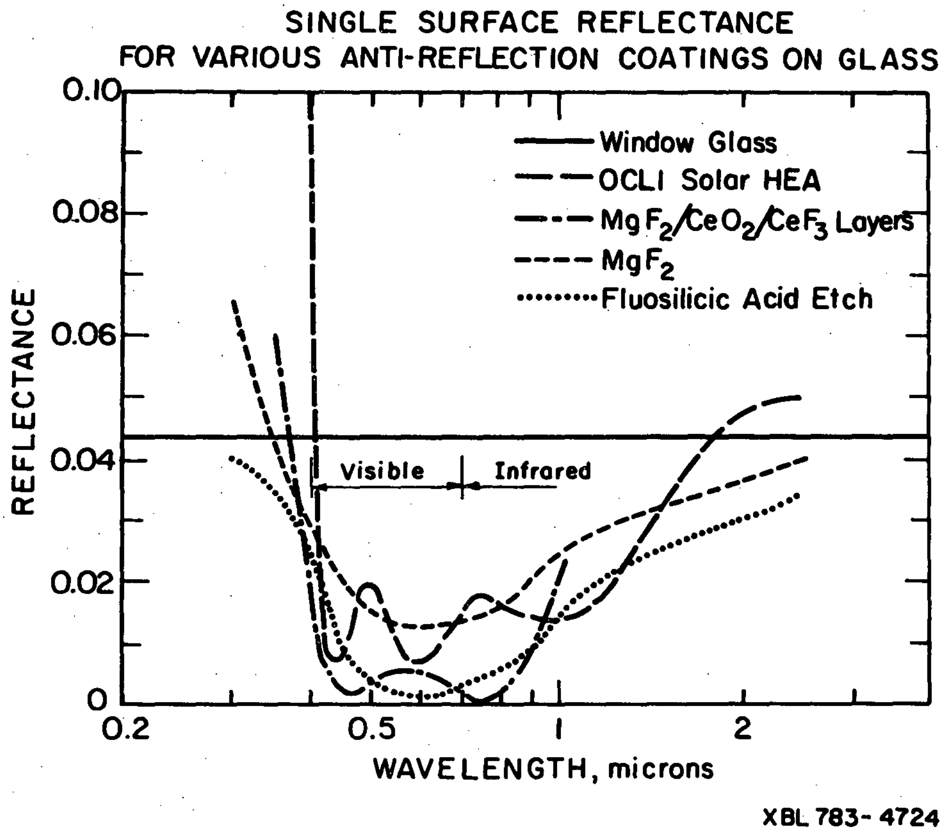

Fig. 29. Reflectance of various antireflection treatments for glass (referenced in text).

according to Jurisson [50]. The spectral properties are shown in Fig. 29 for this etching technique. Refinements of the fluosilicic procedure consists of two layer treatments.

Both single dip coatings, antireflection and etching, appear to be the least expensive for the collector cover applications, while the best performing coatings are the multilayer coatings. However, it appears that all the various antireflection coatings need to be evaluated and compared in terms of atmospheric and operational degradation.

8. APPLICATIONS OF COATINGS

By the use of the various coatings discussed previously certain solar energy collection efficiencies can be obtained. The decision to use or not to use a coating is usually an economic one. Since the economic issue is hard to address, due to a constantly changing industry, the following discussion will only cover gains in efficiency by the usage of a particular surface coating. Since an in depth study could be undertaken in the application of various coatings, their parameters and specific characteristics considered, the intent of the following material is to give the reader a "feel" for the relative trade-offs between coating classes.

Two cases will be treated: a standard double glazed flat plate collector operating at 93°C (200°F) with 21°C (70°F) ambient, and a parabolic collector operating at 315°C (600°F) with the same ambient temperature. These collectors will operate at these fixed temperature requirements while the efficiency is allowed to change due to only additions of intervening coatings. In each case the assumption is made that sufficient amount of incident solar energy is available to maintain the end-use temperature. So in this way losses can be directly interpreted as declines in efficiency. The flateplate collector might be viewed as being used in a residential or commercial application for heating water, while the concentrating collector might be supplying steam for an industrial process.

In Fig. 30 a flat plate collector is depicted. Part (a) shows a typical standard non-selective coating with a = 0.92, e = 0.92 (93°C). By use of an antireflection film on all cover plate surfaces

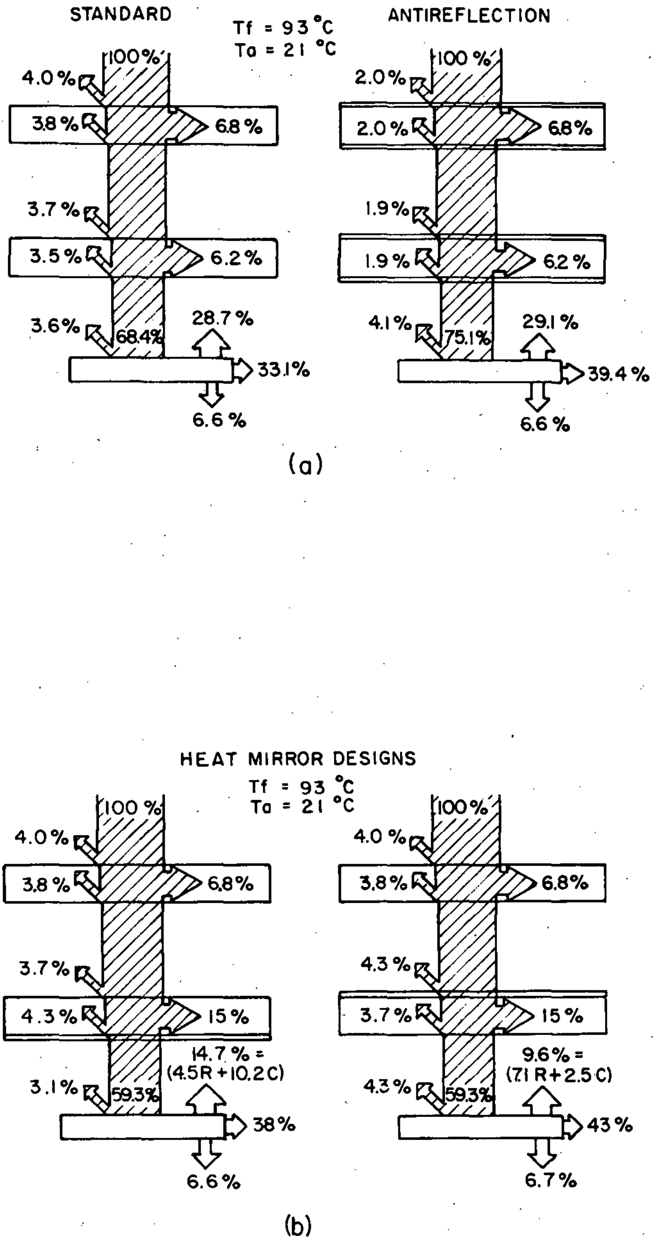

Fig. 30. The effect of various coatings on collection efficiency (Tf) for a flat plate collector operating at 93°C (200°F) with ambient temperature (Ta) of 21°C (70°F). (a) Standard flate plate collector compared to one with antireflective coatings. (b) Two types of heat mirror placements. (c) Standard flat plate collector shown in contrast to one with selective absorbers. Notation: (R) stands for reflection, (c) stands for convection losses. (After Winegarner [52]).

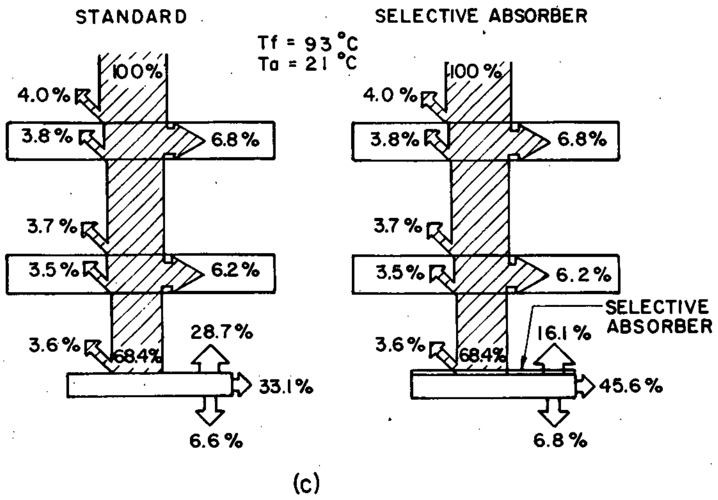

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Fig. 30. Cont.

reflection losses can be reduced by 7.2% and the net collection efficiency inceased from 33.1% to 39.4% indicating a total increase of 6.3%. By application of a heat mirror coating with t = 0.85, e = 0.14 on the fourth collector cover surface (Fig. 30b) the net efficiency can increase from 33.1% to 38% corresponding to a net increase of 4.9%. If the heat mirror is applied to the third surface cover an additional gain is seen as 5%, giving a net gain of 9.9%. Now, a selective absorber, a = 0.90 and e = 0.10, is put in place of the black standard coating. The net gain from this design would be 33.1% increased to 45.6%, or 12.5%; the highest net gain of any particular coating. If antireflective coatings were also used this net gain would be about 19% over that of a black standard collector design. If an anti-reflection coating were used with the heat mirror one might expect a total gain of about 15.5%, above a standard flat plate collector.

Now let us consider a concentrating collector with mirror reflectivity of 85% as a depicted in Fig. 31. In Fig. 31a a standard parabolic trough collector is shown with a black absorber coating--a = 0.95 and e = 0.95 (315°C). The net collection efficiency for the evacuated type glass enclosed absorber is about 40% for an operating temperature of 315°C (600°F). If an antireflection coating is used on the exterior of the glass tube a net increase of 2.1% is obtained. The largest gain comes from the use of a selective absorber coating--a = 0.95, e = 0.06 (315°C). The efficiency of the collection becomes 62.5%, a net increase of 22.5%. If an antireflection film were also used the net increase would be about 24.5% over that of the black absorber.

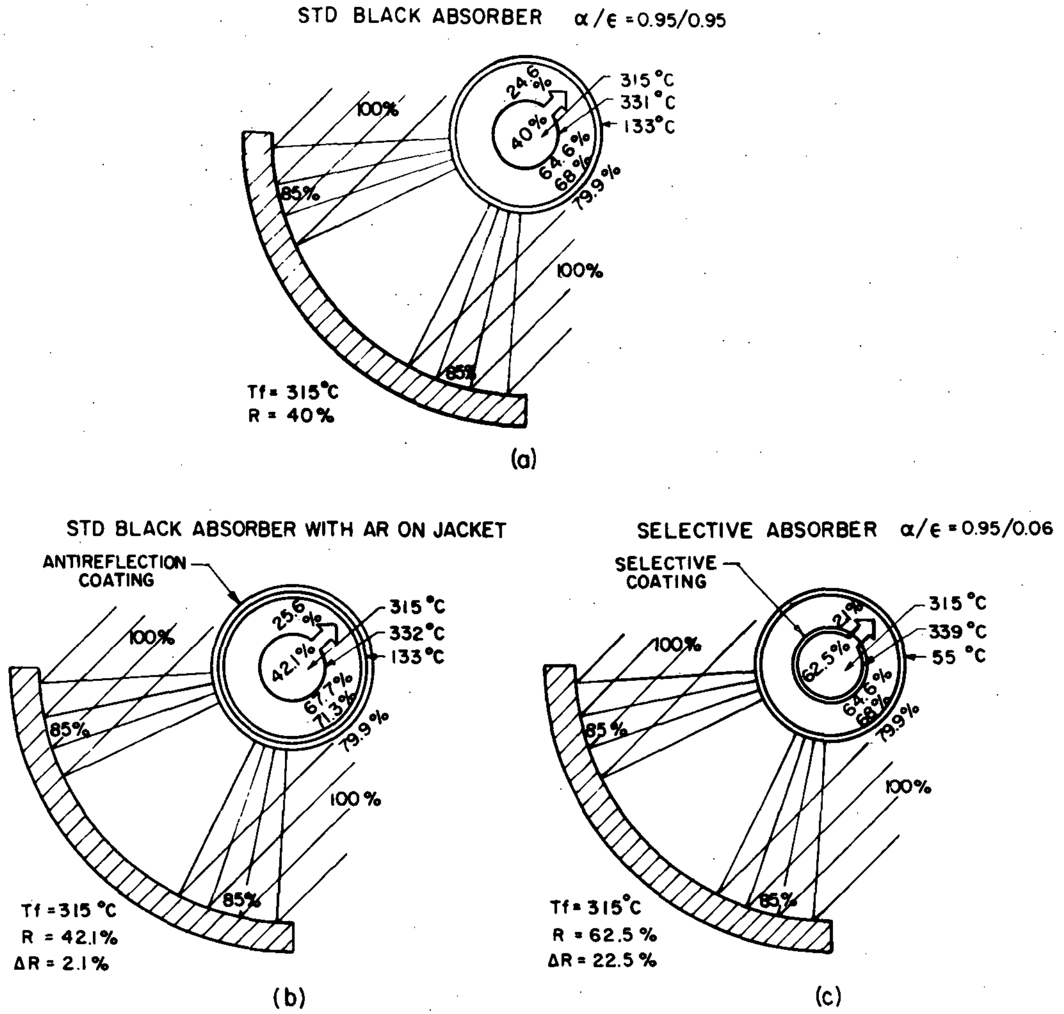

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Fig. 31. The effect of various coatings on collection efficiency for a parabolic concentrating evacuated collector operating at 315°C (600°F) with ambient temperature of 21°C (70°F). (a) Non-selective black coating. (b) Non-selective black coating with antireflection coatings. (c) Selective coatings. Notation. (R) Net collection efficiency, (ΔR) change in collection efficiency over that of a standard black absorber (after Winegarner [44]).

As a result it is obvious that at higher operating temperatures and by the use of a concentrating parabolic collector a selective surface becomes a very important consideration. Increases in net efficiency can range from 12-22%. For double glazed flat plate collectors the use of a heat mirror (9.9%) rivals that of the selective surface (12.5%). The use of antireflection coatings gives a net gain of 2% per surface, on the average. Whether a particular coating should be used or not would depend heavily upon the economics of the various alternatives, that is in some cases all coatings may be cost effective and in other cases, such as possibly a swimming pool heater, few at all would be cost effective. Seen even in this light, the use of coatings at elevated temperatures and high collection cost is almost a mandatory requirement.

9. CONCLUSIONS AND RECOMMENDATIONS

As a result of this study the following general conclusions and recommendations appear to be valid for the use of coatings for enhanced photothermal energy collection.

1. There are many promising cost effective coatings for usage in solar energy. A few for low temperature use (150°C-300°C) are copper oxide chemical conversion, black paints, black nickel and black chrome electrodeposits. Although black chrome appears to be the most stable, these coatings are favored because the capital equipment already exists and several of the processes have been used for years, although not for solar energy. For higher temperatures (300°C to 500°C and beyond), the multilayer AMA coating, U. of Arizona silicon absorber, tungsten dendrites, plasma sprays, and fractory paints appear to be good absorber candidates. Also, there appears to be a gap between the temperature application range 350°C to 500°C. Most selective absorbers operate up to 350°C or perform beyond 500°C; very few exhibit a temperature stability limit around 400°C, which would be adequate for most applications. There are still a multitude of coatings and processes which are promising but not enough research has been performed to adequately characterize them.

Even though many promising coatings exist, very little is yet known about their operation and possible degradation in real operating environments. It is expected that the presence of moisture, heat, and atmospheric contaminants may disqualify many potential absorbers. Unfortunately, only a minute amount of information is available on the degradation of these coatings. Currently it is hard enough to obtain temperature stability information in dry air for a particular coating.

2. Tandem absorbers appear to be very popular and well suited for solar energy collection at moderate temperatures. Natural oxidation of metals shows promise of being a very simple selective absorber.

3. For electroplating there is a possibility of strip plating thin metal and bonding this material to collector plates, the strips transported and sold in rolls. This technique is being used already on a small scale for black chrome. Automated sputtering also offers the advantage of accepting large work surfaces, with the ability to deposit a wide variety of substances. Improvements in vacuum systems and large scale production vacuum deposition techniques are also necessary for low cost and high yields.

4. Selective materials may be created by surface roughening or by refractive coating structures. Also, use of composite resonant structures can result in solar selectivity.

5. Coatings should have their spectral properties designed to the optimum with respect to specific operating conditions and temperatures. Certain coatings should be matched to a particular collector design and end use. In many cases a,e values should be designated as a function of temperature, to match end use temperature.

6. Over coating of non-selective paints by an infrared reflecting coating such as tin oxide can improve solar selectivity.

7. Multilayer coatings frequently exhibit corrosion and interdiffusion problems at elevated temperatures. An example that these problems may be overcome is demonstrated by the AMA absorber.

8. A solution to a manufacturing problem which must be worked out is the production of reproducible a and e coatings values, along with collector standards and specific efficiency rating systems, including the measurement of optical parameters of various coatings provided by the manufacturers.

9. Coatings are very important in terms of collector durability. If a coating degrades, so does the entire system. In a commercial or industrial application solar collectors can be maintained on a routine schedule. But for the homeowner this is seldom possible. what is needed are coatings which will not optically or thermally degrade much more than a few percent over the lifetime of the collector, possibly 10-30 years. In other words, hopefully the coating would not be the limiting factor of collector lifetime. These coatings would have to withstand the most severe conditions such as summer stagnation and temperature cycling for many cycles. Stagnation can occur early in a collector's lifetime, perhaps as during the construction of a collector system. Once in operation solar collectors can stagnate when the system malfunctions and stagnation temperatures can exceed 200°C. Stagnation temperatures should be known, as an engineering design parameter for specific coating and collector designs. In general it is important that the coating be able to survive several weeks (months) of stagnation temperatures. Currently little is known about the effects of these short term high temperature excursions on coating

properties. This remains as one of the most significant areas of investigation. Humidity and potential outgassing of sealant and insulation used in collectors can have an adverse effect upon coating life and collector performance. All of these points need to be pondered and evaluated before a collector can exhibit the necessary reliability.

10. A formal materials cost analysis is needed for both selective and non-selective surfaces including both antireflection and heat mirror coatings. Among the popular selective and non-selective coatings the price range is from \$2.70-\$19.00/m^2 and for painted coatings the prices can be as low as a questionable \$0.22/m^2. The black chrome coatings range from \$7.50-\$12.00/m^2 which appear to be fairly typical of electroplated coatings. Commercial vacuum deposited selective coatings can cost from \$16.00-\$38.00/m^2 and upward. All of these numbers are just estimates; they do not represent high volume production with possible automation.

11. Work should be performed upon the toxicity of the various coatings used in collectors. Another concern is with possible flamability and toxic by-products of combustion generated from the burning of solar collectors in fires.

12. The amounts of energy used to make various coatings and collectors should be evaluated. For many coatings heat treatments or hot fluid baths are used. Electricity is needed in many cases for vacuum deposition, CVD, sputtering, plasma deposition and electroplating, cleaning and chemical conversion use whater in the 100°C range, which might be, in turn, supplied by solar collectors!

13. It is also necessary to consider the availability of raw materials used for coatings and collectors. Some materials are in very short supply or have already been allocated for specific usage in other manufacturing areas. At present, some metals such as chromium and tin are imported in the U. S. Changes made by our suppliers could have an impact upon our society both economically and politically.

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