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Review
Materials for photothermal solar energy conversion

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Commerically or potentially available selective and non-selective absorber surfaces for solar heat collectors are reviewed and the state-of-the-art of solar collector corrosion processes is outlined. The review of available published literature has indicated that a lack of quantitative information exists, relative to corrosion of collector surfaces. Available information (mostly qualitative) on durability aspects and corrosion of solar receiver surfaces is described to indicate potential corrosion problem areas and corrosion prevention possibilities. An outline of appropriate durability tests is presented.

1. Introduction

The utilization of a low intensity energy source, such as the normal solar radiation, for the heating of various fluids (water, air, special heat-transfer media) or for the production of steam, requires an effective collection and retention to be economically feasible. Therefore, all collector designs utilize a specific receiver system to absorb the incident solar radiation. In some cases, the energy collection may further be enhanced by concentrating the incident radiation onto the receiver system, which results in higher operation temperatures (up to 300 or 500° C and beyond for parabolic concentrator(s)). Most collectors, however, are of the non-concentrating type and operate at rather modest temperatures (generally $< 100°$ C; flat plate solar collectors) except for summer stagnation periods where temperatures up to about 200° C may be reached.

Different concepts of the solar receiver system have been developed in the past. Conversion of the incident solar radiation into heat is normally achieved by either direct absorption in a heat transfer fluid, which is flowing through transparent channels (black liquids [1, 2] or solid/gas suspensions [3]) or, as is mostly the case, indirectly by means of some kind of blackened or specially developed absorbing surface from which the heat is collected and conducted to the heat transfer fluid. Unless manufactured from a self-coloured material such as a black plastic, the latter receiver system usually consists of a base metal plate finished on its top (exposed) side with a specific solar absorber layer.

There are many candidates for these solar absorber layers and a lot of them can be applied onto a variety of structural absorber plate materials, such as carbon steel, galvanized steel, stainless steel, copper, aluminium etc. The most common type of solar absorber coating consists of ordinary non-glossy heat-resistant black paint. A number of proprietary paints for solar heat collectors are available (see Section 3). These coatings generally offer sufficient absorption of the high energy solar radiation but also act as good re-radiators in the thermal-infrared spectral region, thus losing a large amount of the initially captured energy (Fig. 1a). The radiation losses, of course, are mainly a problem at more elevated operating temperatures of the solar collector. For optimum efficiency the

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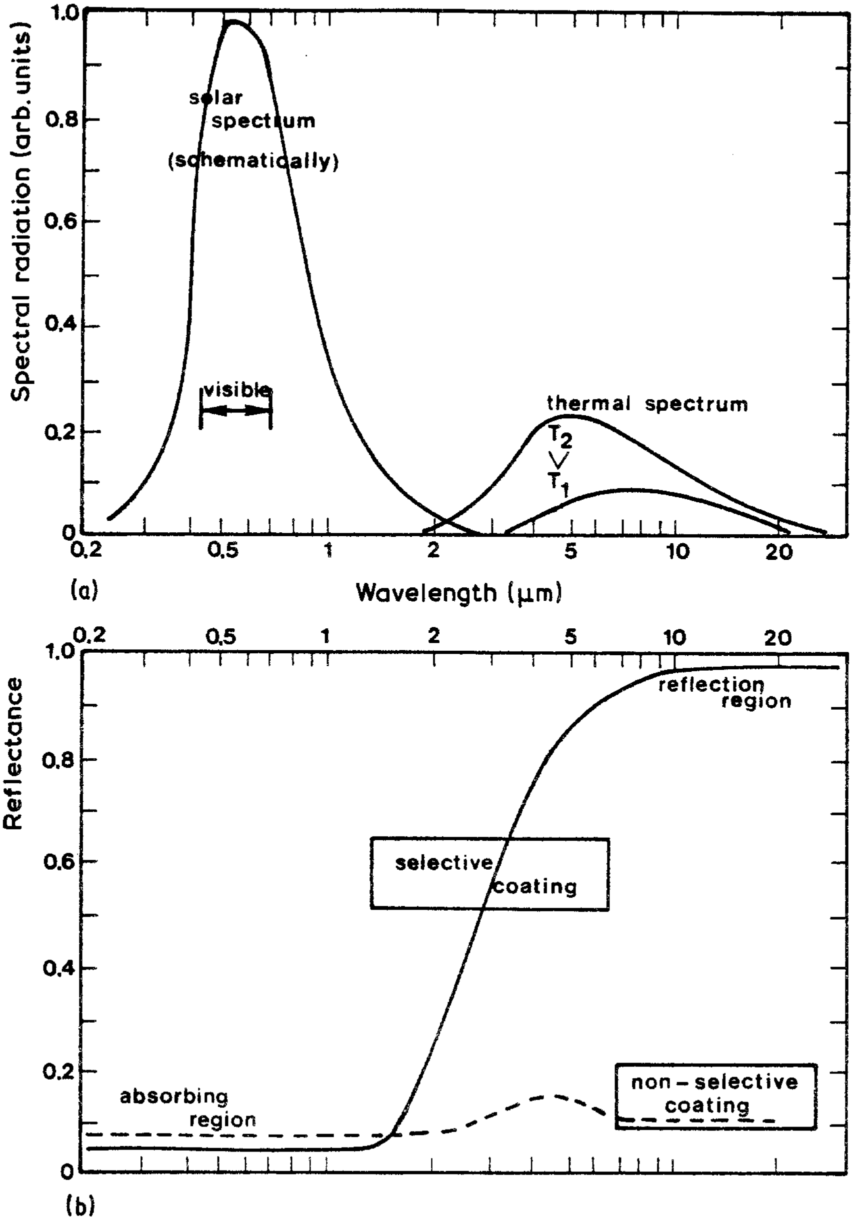


Figure 1 Solar and thermal spectra (a) together with the typical spectrometric curves of a selective and a non-selective absorber coating (b).

solar absorber should possess the maximum possible absorptance in the solar spectrum while exhibiting a minimum infrared emittance. This may be accomplished by using a so-called "selective" absorber coating (Fig. 1b). Selectivity is produced by a substance that exhibits optical properties which vary greatly from one spectral region to another. A solar selective surface efficiently captures solar energy in the high intensity visible and the near-infrared spectral regions while maintaining poor thermal-infrared radiating properties. Accordingly, a selective surface will absorb and retain a high amount of energy from the sun, while a non-selective surface will loose much of its absorbed energy by re-radiation. Good selective absorbers have absorptances (α) as high as 0.95 and emittances (ϵ) below 0.1 at the working temperature of the absorber surface, thus providing high α/ϵ ratios. For non-selective surfaces α/ϵ nearly equals unity.

Despite the considerable attention which has been focused during the past few years on the development of surface coatings with superior optical properties and the improvement of the process efficiency in terms of absorbing a maximum energy flux from the sun, less attention has been given to the durability aspects of the different materials. In order for a solar collector to have a high long-term efficiency, however, longevity and a minimum of maintenance are prime requirements and degradation modes of the various components should be well understood. Although material and degradation problems must be considered in relation to all components used, problems concerning the absorber plate of the collector are obviously most critical because of their immediate impact on the energy conversion efficiency.

In most receiver designs, the absorber surface is protected by a transparent cover (glazing), which reduces convective heat losses. In the most advanced designs, this cover provides a means to control the atmosphere to which the absorber surface is exposed. In less advanced designs, however, the glazing may trap and concentrate undesirable elements such as moisture (including condensation) and atmospheric pollutants (SO_2, CO_2, Cl^-, NO_x etc.) or outgassing products of insulation and resin-bonded materials. This may create an unexpected corrosive environment for the absorber surface which in either case is also subject to a series of other hostile conditions: elevated temperatures, continuous thermal cycling, thermal shocks and maybe ultraviolet irradiation.

It can be expected that selective absorber layers, with their exacting optical properties, are potentially most sensitive to degradation. Unfortunately, the degradation mechanisms and durability properties of these surfaces are often poorly understood. Some of the systems are known to be more chemically and thermally stable than others, but there are large gaps in the stability data for a large number of the systems. In an inert environment, the principle degradation mechanisms are interdiffusion between different layers or phases of the absorber and changes in surface morphology. These degradation mechanisms would be minimized by using refractory metals and compounds for the absorbing layer and using refractory materials or diffusion barriers for the underlayer. In a reactive environment, the choice of materials is much more restrictive since internal chemical reactions can change phase compositions and interfacial reactions can lead to loss of adhesion. Detailed, reliable data on this subject are hard to obtain at the present time. The same can be noticed about the corrosion behaviour of many non-selective coatings under specific solar collector conditions.

The scope of this report is to give a survey of commercially available or potentially available absorber surface coatings and to put forth accessible data about durability and deterioration (corrosion) phenomena. Most of these data will only be very qualitative and for the large majority of the systems, a complete absence of durability data is noticed.

2. Selective solar absorber surfaces

2.1. Principles for obtaining solar selectivity

Spectral selectivity may be based on different physical concepts and selective solar absorbers may be fabricated from a number of materials or material combinations by a variety of techniques. Surveys have for instance been published by Duffie and Beckman [4], Peterson and Ramsey [5], Meinel and Meinel [6], Tabor [7], Hahn and Seraphin [8], Seraphin [9], Sievers [10], Lampert [11, 12], Mattox and Sowell [13], Koltun [14] and Dickinson and Cheremisinoff [15]. Fabrication techniques mostly include some coating or surface conversion process. Examples include electro-, electroless- or strip plating [16], vacuum or gas evaporation, chemical vapour deposition, inert or reactive sputtering. Others include chemical or plasma spray, application of paints or enamels and the chemical (e.g. oxidation), electrochemical or physical (e.g. ion bombardment) surface conversion. The physical concepts or mechanisms for obtaining spectral selectivity and the corresponding selective surfaces may be generally divided into four different groups:

(a) intrinsic spectral selective materials,
(b) absorber/reflector tandems,
(c) wavefront discriminators,
(d) interference stacks.

Selectivity of an actual surface, however, often depends on a combination of different effects.

2.1.1. Intrinsic spectral selective materials

Very few bulk materials possess a pronounced degree of intrinsic spectral selectivity. Well known examples are Cu_2S and HfC. Pure tungsten is one of the most wavelength selective metals. Metals, however, normally show a transition in their reflectance behaviour too early in the radiation

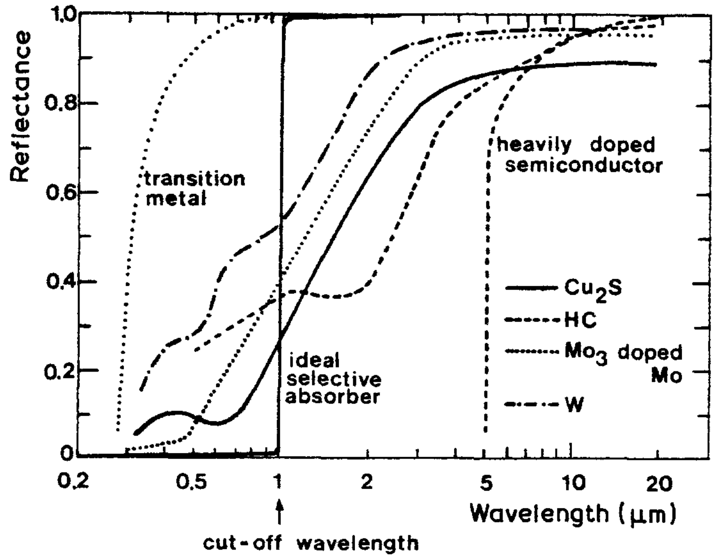


Figure 2 Spectral reflectance of an idealized selective absorber compared to an idealized metal and a heavily doped semiconductor, together with the reflectance curves for some intrinsic solar selective materials: metallic tungsten, MoO_3 doped molybdenum, Cu_2S and hafnium carbide (after Lampert [11, 12], Seraphin [9] and Meinel and Meinel [6]).

spectrum (Fig. 2) and for most semiconductors this transition lays too far in the infrared. Creation of internal scattering centres in the metallic lattice (e.g. MoO_3 doped molybdenum) or making a semiconductor highly degenerate, might provide the possibility for adjusting the transition frequency. Unfortunately, many unresolved complications [8, 9, 17, 18] limit the number of actual available intrinsic absorbers. Some of them, known as heat mirror materials (e.g. LaB_6) will be discussed at the end of this chapter. Other examples include a number of carbides or nitrides of the transition metals (see Section 2.2) and may be combined into a more complex "tandem absorber" system.

2.1.2. Tandem stacks (absorber/reflector tandem)

A "tandem absorber" system – more rigorously: an absorber/reflector tandem – generally consists of a combination of two materials, each having a specific optical function to form a bulk absorber with solar selective properties. Absober–reflector tandem coating systems make use of a highly infrared-reflecting metal substrate over which a coating is deposited having high absorptance at solar wavelengths (i.e. it is black), but which is transparent to long-wavelength "black-body" radiation (Fig. 3). Thus, the tandem has the high solar absorptance of the black exterior deposit and the low thermal emittance of the metallic reflector substrate. This

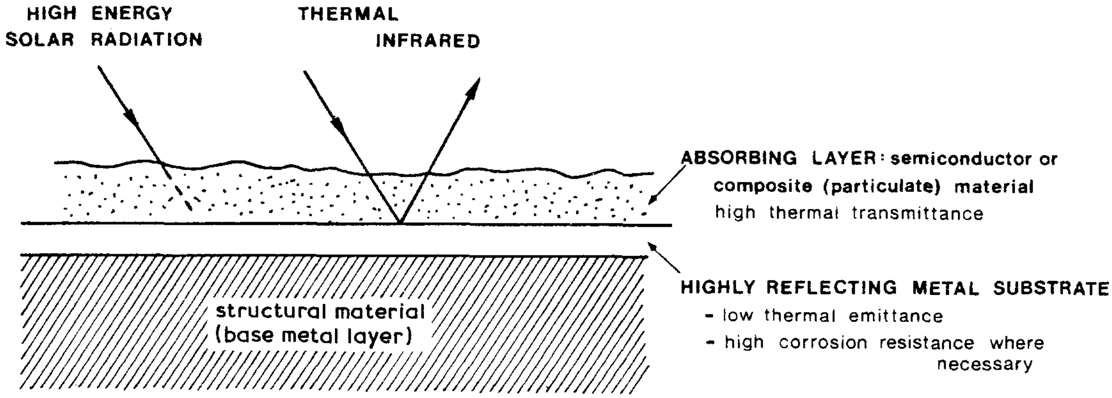


Figure 3 Typical selective solar absorber coating, containing an outer absorbing layer and a low-emittance substrate (absorber–reflector tandem).

selective absorber coating configuration should preferably have a high thermal conductivity to keep the coating surface temperatures as low as possible.

The low thermal emittance underlayer surface is generally a metal such as copper, nickel, molybdenum, silver, aluminium, carbon steel, stainless steel or zinc, which have thermal emittances of about 0.1 at 300° C [13] and which may provide corrosion protection for the underlying structure where necessary. These metal coatings may be deposited by a number of techniques such as electroplating, sputter deposition, vacuum evaporation, or may be the structural material of the solar receiver. For non-corrosive environments, this underlayer may be very thin, but where the underlayer must provide corrosion protection for the structure, the layer must have an appreciable thickness which will depend on the service conditions.

High absorption of the exterior coating may be either intrinsic in nature (material with high extinction coefficient), or geometrically enhanced, or, as is usually the case, it may be a combination of both.

An intrinsic high absorption of the solar radiation may for instance be obtained by using semiconductors, such as silicon, germanium and PbS, with an optical absorption edge near 2 μm. For semiconductors, solar absorption is a result of the interaction of photons having energies greater than the semiconductor band gap: the coating absorbs the photon as a result of raising the materials valence electrons into the conduction band, and photons of less than the band-gap energy are transmitted through the materials unaffected. Since these semiconductors all have high refractive indices, antireflection surfaces must be used to prevent excessive reflectance losses (e.g. surface morphology which gives radiation trapping or application of additional surface layers) [13]. There are, however, numerous other successful semiconductor/metal combinations (e.g. CuO_x on aluminium), one of the simplest examples being an oxidized metal, where the oxide provides the necessary solar absorbance. The latter type may, on the other hand, show some more or less pronounced relationship with a different kind of absorbing layer, namely particulate or composite coatings.

In these cases absorption is enhanced by textural effects (resonant scattering [12, 15] and reflective scattering where high absorption is obtained by multiple reflections). Textural effects based on resonance phenomena are affected by both size and optical properties of surface particles or the surrounding matrix and depend upon the material and its morphology in the subwavelength size range [19–21]. Reflective scattering, on the contrary, is only determined by pure geometric properties of the surface particles, in the order of the wavelength of solar radiation (500 nm; see Section 2.1.3). Well known examples of particulate coatings are electroplated "black chrome" (chromium particles in a Cr_xO_y matrix in a rather open structured coating [22–25]; Fig. 4), "black nickel" [26, 27], copper oxide, powdered semiconductors, certain dispersions of metal particles in a metallic matrix and many cermets (ceramic–metal composites), produced by inert or reactive sputtering, in which very small metallic phase particles (5 to 10 nm) are dispersed in an amorphous dielectric matrix (e.g. Al_2O_3–Cr, ZrC_x etc.).

An interesting variant on the principle of the previously described absorber/reflector tandem system is the so-called "inverse tandem absorber", in which an overlayer of a selective transmitting material (heat mirror or selective window material) is coated on top of an absorbing substrate. In this configuration the top layer reflects the infrared wavelengths while the bottom layer absorbs the high energy visible light. This system thus works in reverse of the regular tandem absorber. An example is In_2O_3 on silicon [28]. In_2O_3 appears transparent in the visible range but acts like an infrared reflector, while the buried silicon layer performs as a solar absorber.

2.1.3. *Wavefront discriminators*

Solar selectivity of a metal surface may be produced by purely geometric means. Surface irregularities such as grooves and pores with dimensions large as compared to the wavelength of the incident radiation simply increase the solar absorptance and, to a less extent, the infrared emittance by multiple reflections [29] (Fig. 5). Irregularities with dimensions comparable to the cut-off wavelength (maximum wavelength to be absorbed) only increase the solar absorbance and have little effect on the thermal emittance [20–32]. This different optical behaviour in the visible and infrared is explained by "wavefront discrimination" effects (Fig. 6). For visible wavelengths, which are

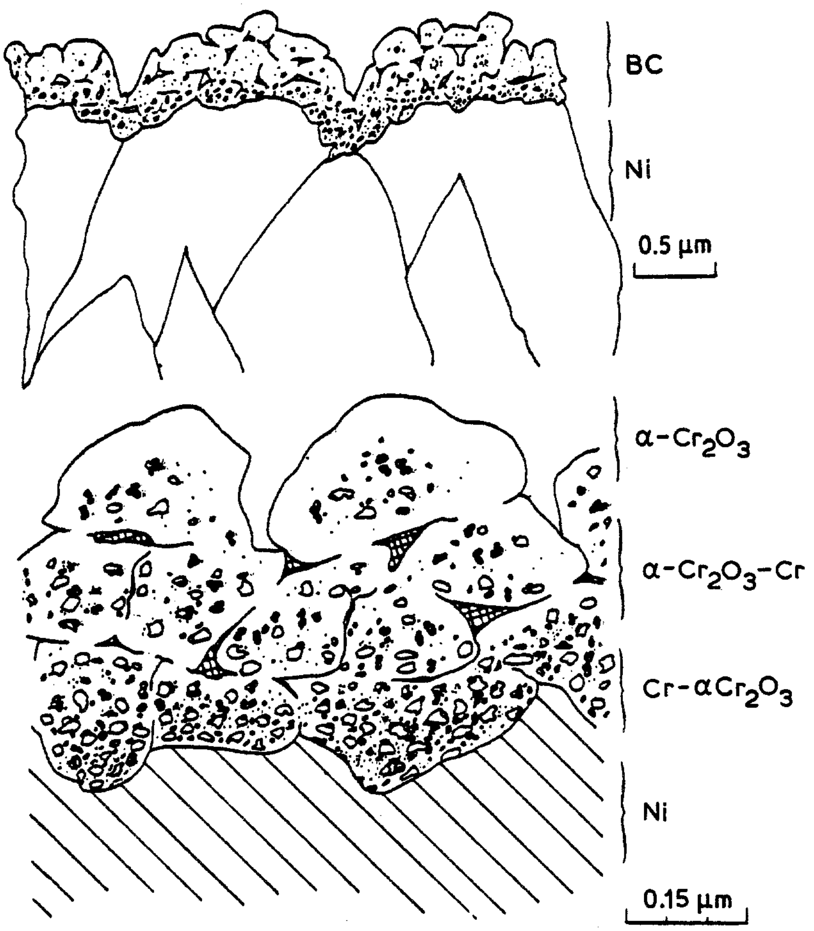


Figure 4 Schematic cross-section of black chrome [159].

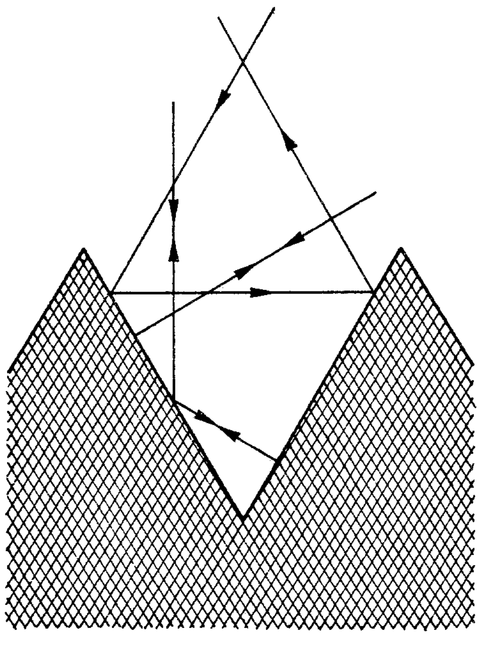


Figure 5 Shaped surfaces on the absorber substrate increase the net absorptance of the coating through multiple reflections (after Meinel and Meinel [6]).

small compared to the actual irregularities, the surface looks rough and radiation may be trapped through multiple forward reflections and partial absorptions in the micro-cavities. For the thermal infrared, however, the wavelength is larger than the dimension of the surface roughness and the surface will therefore appear smooth and mirror-like and radiate as a flat surface in the longwave spectrum. The metal will thus show its bulk properties of low infrared emittance.

Needle-like, dendritic or porous microstructures are typical examples of wavefront-discriminating textures. A schematic representation of the radiation trapping with dendritic selective absorbers is shown in Fig. 7.

A review of experimental methods for the preparation of selectively absorbing textured surfaces has been published by Pellegrini [33]. Typical examples are thermal vapour deposition, chemical vapour deposition, anodizing or surface etching.

2.1.4. Interference stacks

Multilayer thin films known as interference stacks

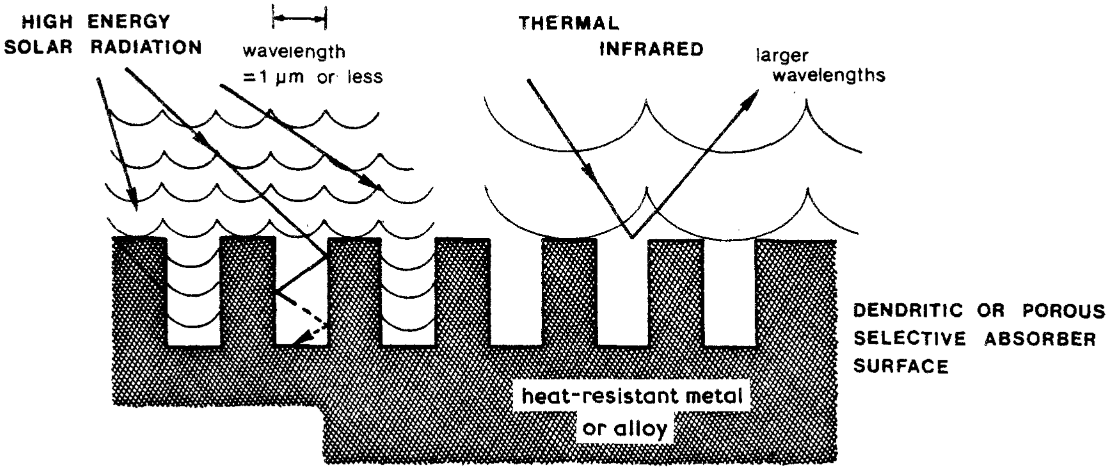


Figure 6 Wavefront discriminating effect on textured surfaces [33] (schematically; depth of the cavities not shown on the real scale).

are complex 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 by phase interference (Fig. 8). In the case of naturally selective materials or tandem absorbers the desired optical effect is generally produced by a single pass through the optically active medium, or the return pass after reflection by the underlying mirror surface. In the case of an interference stack the desired effect is the net result of a multiplicity of passes through the dielectric portion of the stack lying between two reflective surfaces, the upper one of which is partially transparent. Careful tuning of the layer thicknesses and variation of optical constants with wavelength is necessary to get absorption of particular wavelengths of solar energy by multiple reflection in the dielectric–metal layers. Other wavelengths not corresponding to the absorption frequency of these layers are reflected. The basic concept for a four-layer interference stack is illustrated in Fig. 8.

The thin metal film usually is only approxi-

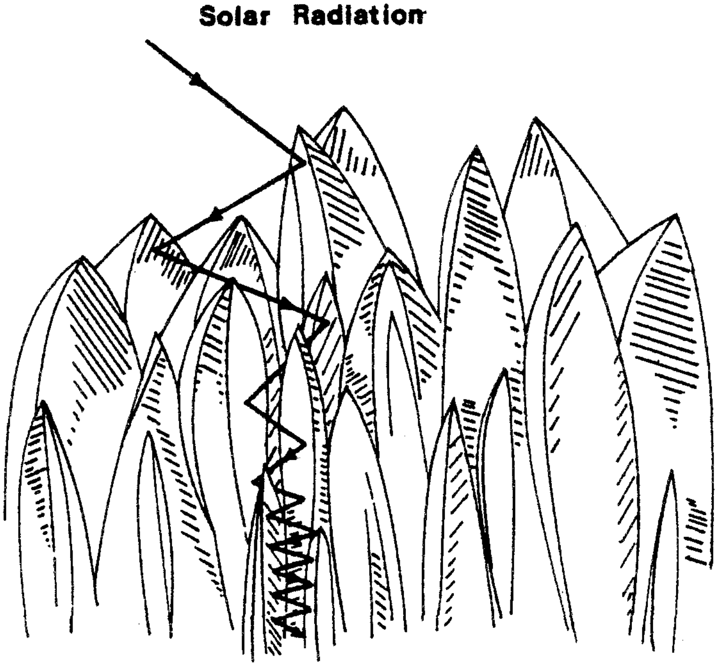


Figure 7 Schematic representation of a dendritic selective surface. Incoming radiation can average up to fifty reflections before being completely absorbed [12].

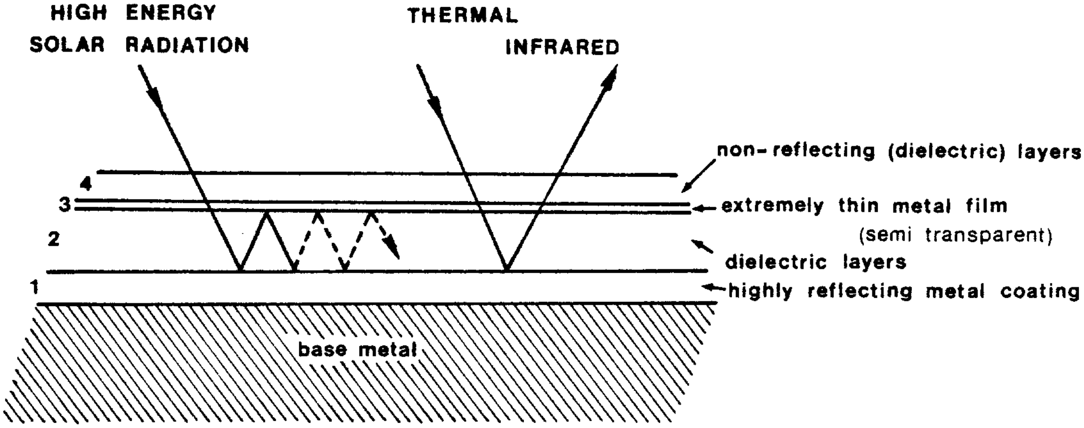


Figure 8 Schematic cross-section of a four-layer interference stack consisting of two dielectric quarter-wave layers separated by a thin, semi-transparent metal film (after Meinel and Meinel [6]).

mately 5 to 10 nm thick, to appear semi-transparent to the incoming radiation. Being such a thin layer the actual composition is not well defined. It is believed that most of the incoming energy is attenuated in this metal layer and that "quantum size effects" may help to describe the actual process of absorption response [12].

It should be noticed that the dielectric layer between the metal surfaces need not exhibit intrinsic absorption characteristics in the solar spectrum for the stack to be an effective absorber, but often multilayer interference stacks appear not totally unlike the complex multiples of the tandem systems described previously. Layer thicknesses, however, are very different.

Fabrication techniques of these layered structures comprise evaporation, sputter deposition or electroplating. A successful example is the Al_2O_3–Mo–Al_2O_3 (AMA) [5, 34] interference type selective absorber coating (see Section 2.2). The topmost Al_2O_3 coating (80 nm) acts as an antireflection coating while the molybdenum (or MoO_x) (10 nm) and the underlying Al_2O_3 (300 nm) act as the absorber. This layered structure is deposited on a molybdenum or stainless steel underlayer.

2.2. Survey of available selective surfaces

The major part of all known selective surfaces consists of an absorbing coating on a metal substrate, the coating providing the high solar absorptance and the metal providing the low thermal emittance (tandem absorber system; see Section 2.1.2). The first selective surfaces were mainly metal oxide and sulphide layers coated onto various metals. Important practical examples are black nickel (NiS–ZnS) and black chrome (Cr–CrO_x), copper oxide or "black copper" (CuO_x or CuO), iron oxide (Fe_3O_4) and cobalt oxide (CoO_x).

Black nickel layers consisting of a Ni–Zn oxide/sulphide complex were introduced by Tabor [26] in the later 1950s and have been in use in Israel for many years. They can be obtained by chemical conversion of a zinc-coated substrate (zinc-plated mild steel, galvanized iron, zincated aluminium, "Zincalume" – a mild steel coated with a zinc/aluminium alloy) [36–38] or by electrodeposition from Ni + Zn sulphate baths [26, 27, 39, 40], usually – although not necessarily [41] – over an undercoat of nickel or zinc. By changing the plating current density during the electrodeposition process, a succession of layers with different characteristics may be obtained (multilayer coating) [42, 43] and optical interference phenomena might be induced. The optical response of an actual nickel-black coating therefore often resembles the behaviour of an optical interference stack, with a characteristic double minium of the reflectance curve in the visible wavelength region (Fig. 9).

Also cobalt oxide [44–50] and black chrome (CrO_x–Cr composite, cf. Section 2.1.2) layers are produced by electrodepositive means. A large number of experimental or commercial deposition baths have been developed for producing black chrome coatings [44, 51–60]. Well known proprietary baths are for instance the Chromonyx (Harshaw Chem. Corp./Corillium Corp.) or Solarchrome process and the Du Pont Co. bath. Although the base metal could be copper, aluminium (bright or zincated), stainless steel and bare or

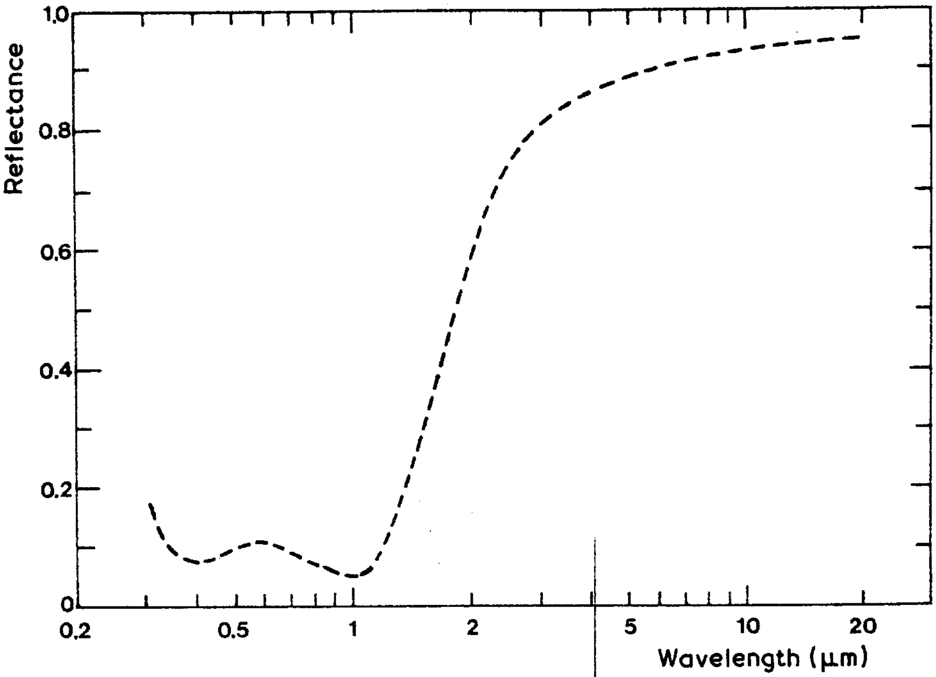


Figure 9 Spectral reflectance for black nickel developed by Tabor [26].

galvanized carbon steel, in many cases a nickel layer is to be preferred as the substrate material (cf. Section 4). Applying a nickel coating might, however, cause an important increase of the initial cost per unit of collector area.

Other preparation methods for $Cr-Cr_2O_3$ composite coatings have also been described, e.g. sputtering [61] or a chemical blackening (dipping) process for stainless steel or nickel plated mild steel [62].

Copper oxide layers [5, 63–65], which have been used to a considerable extent in Australia, have been produced on aluminium, by spraying or dipping in copper-containing solutions and a chemical or thermal treatment [66, 67], or on copper metal, using a chemical or thermal oxidation process [68]. Commercial chemical oxidation processes comprise for instance the Ebonol–C process (Ethone Co.). The latter techniques can, of course, also be applied on any other base metal after electroplating with a thin layer of copper.

Also iron oxide layers are principally produced by chemical oxidation [69, 70], although thermal [35] or electrochemical means might provide an attractive alternative.

All the above mentioned surfaces have solar absorptances of about 0.90 and thermal emittances at 100° C of about 0.1 to 0.3. Their long-term thermal stability confines their application to operating temperatures in the range 150 to 200° C. Possible exceptions are black chrome [23, 71] and cobalt oxide [50] which seem to remain stable well above 200° C.

Recently, this class of selective surfaces has been extended with some new materials. Transition metal carbides and nitrides, produced by reactive sputtering, are reported to be stable up to 600° C in vacuum and exhibit a very low emittance of 0.02 to 0.06 [72, 73]. Also, a very good selectivity is obtained by chemical [74, 75] or by thermal [76, 77] oxidation of stainless steel. Electrochemical treatment at elevated temperatures would, however, provide many more possibilities of surface compositions and structures that can be obtained [78].

A different class of selective surfaces is formed by intrinsic semiconductor coatings on a metal base, the semiconductor band gap providing the required wavelength discrimination (cf. Section 2.1.2). A suitable material is silicon, both in the crystalline and the amorphous state, deposited by chemical vapour deposition (CVD) [17, 79–81]. These coatings are extremely stable (up to 800° C) and have absorptances of about 0.8 and emittances at 500° C well below 0.10. Other materials are germanium, deposited by vacuum evaporation [82, 83] and PbS, deposited by gas evaporation [83, 84]. Since the optical properties of these semiconductor-coated surfaces are relatively insensitive to the coating thickness, selective paints consisting of semiconductor particles in a polymer binder have received considerable attention [64, 85–87]. Although such paints are attractive owing to their ease of fabrication and application and their repairability, the present use is limited because of the relatively high emittance due to the optical properties of the binder (absorption bands in the infrared region). Candidate pigment materials include Bi_2S_3, CdTe, CuS, germanium, silicon and PbS. The most promising binders identified to-date are the silicone resin and aliphatic polymers (polyethylene, polypropylene, polyisoprene and polyamide) [88].

Another approach for designing solar selective paints is to use a coated metal flake instead of semiconductor particles in the paint composition. In this way the selective effect is created as a distributed tandem, with each particle serving as an individual tandem absorber. Recent research has documented this effect [89] and the concept seems to be extremely interesting for the development of cost-effective selective absorber coatings.

A very good selectivity can be obtained by using a multilayer interference stack, consisting of several metal and dielectric layers (cf. Section 2.1.4). Examples are the SiO_2–Al–SiO_2 [90] and the AMA (Al_2O_3–Mo–Al_2O_3) stack [5, 34], the latter being stable at more than 800° C and having an absorptance of 0.85 and an emittance at 500° C of 0.11 (0.07 at 20° C). Other designs have for instance been investigated by Meinel *et al.* [91] (HELIO series) and Long [92]. Because of the sensitivity to slight tolerances in the stack parameters, as well as of the cost and complexity of fabrication, their large-scale use will be restricted.

A quite different approach to obtain spectral selectivity is the use of textural effects (cf. Section 2.1.3). Selectivity due to surface irregularities has been achieved by different authors [33]. Typical examples are dendritic tungsten [93], nickel [94], aluminium [95], rhenium [96] or copper, chromium and nickel deposits with a granular microstructure produced on stainless steel AISI 304 by thermal vapour deposition [97], porous surface structure on Cu–Ni alloys [33] and Al–Ni, Al–Cu or Al–steel compounds [95, 98] and various metal surfaces textured by ion bombardment [99–101]. Textural effects of a different kind are based on resonance phenomena. Embedding small metal particles in a dielectric host is an example of this approach. Practical examples are the "gold-black" [6, 102, 103] or "gold-smoke" [43, 104] deposits and the cermets (ceramic/metal), such as MgO–Au [105–107], Al_2O_3–Ni [21, 108], Al_2O_3–Cr [109], Al_2O_3–Mo [109], Al_2O_3–Pt [110] and Cr_2O_3–Cr (black chrome). The stability of these coatings is generally good (up to 400° C) but their selectivity is only moderate with emittances well above 0.1.

Relatively little attention has been paid to the use of heat mirrors or selective window materials. Only SnO_2 [111. 112], In_2O_3 [113, 114] and LaB_6 [115] have been studied intensively. These semiconducting materials derive their selectivity from the free-electron plasma behaviour. The selective window materials can be used as selective absorbing surfaces by coating them on an absorbing substrate; e.g. SnO_2 on a black enamel substrate [116]. Other different examples, however, might be produced [11].

Table I contains a more extended survey of potentially or commercially available selective surfaces. Availability and properties of practical selective surfaces such as different coatings on aluminium and copper, conversion, sputtered, interference and dendritic coatings, heat mirrors, nickel black, and chrome black, have been briefly commented on by Tabor [7].

3. Non-selective and moderately selective black absorber coatings

Several types of coatings and surface preparations, other than selective absorbers, can be utilized for economical collection of solar energy. This group of non-selective or moderately selective coatings is certainly the easiest to apply and probably the least expensive of all collector coatings. Both moderately selective and non-selective absorbers consist of matt black paints (organic or inorganic), ceramic or organic enamels and certain chemical or electrochemical metal conversion coatings.

There are many types of painted coatings. A compilation of the properties of a few representative paints has been made by Lampert [146]. Table II covers most of them. 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. The essential characteristics of black paints for solar receivers are that they possess high absorptance at angles other than normal incidence, that is, they are optically matt and also have high emittances in

TABLE I Summary of selective solar absorber surfaces

Material coating (/substrate)	Fabrication process	α/ϵ (temperature) (° C)	Thermal stability		Degradation mode	References
			Air (° C)	Vacuum (° C)		
Ge	vacuum evaporation	0.61/0.54 (240)				82, 83, 84
Ge(+ SiO AR)/Al	vacuum evaporation	0.74/0.01 (100)				117, 118
Ge(+ SiO AR)/Ni	vacuum evaporation	0.84/0.04 (100)			(interdiffusion with substrate metal)	117, 118
Ge(+ SiO AR)/Cr	vacuum evaporation	0.90/0.11 (100)	240			117, 118
Ge	gas evaporation	0.91/0.2 (160) /0.5 (350)				85
Ge	paint (silicone binder)	0.91/0.8 (200)				85
Ge + CaF_2 composite	sputtering	0.7/0.1 (500)		> 500		119
αSi/Mo	CVD	0.77/0.1				79–81
αSi(+ AR)/MoO_x	CVD	0.91		> 700	crystallization	120
Si(+ AR)/Ag	CVD	0.80/0.05 (100) 0.07 (500)		> 500		17, 79–81
Si powder coating,		0.9/0.3				121
Si paint		0.83/0.7 (200)				85
Si doped with B	intrinsic					33
Si + CaF_2 composite	sputtering	0.7/0.1 (500)		> 500		119
SiO_2–Ni/Ni	vacuum evaporation	0.92/0.07 (100) 0.12 (400)	–	(400–500)		122, 123
SiO_2–MgO–Ni/Ni	vacuum evaporation	0.9/0.05 (100) 0.11 (400)		(500)		123
SiO_2–Al–SiO_2 multilayer stack	vacuum evaporation	0.95/0.05				90, 124
SiO/Cr/SiO	vacuum evaporation	0.88/0.1	<450			85
SiX_3N_4 overcoat (AR; stabilisation) on e.g. Mo("black moly")	CVD	0.82/0.08 (500)		> 500		125, 126
$ZrBr_2$	CVD	0.93/0.1 (100)	<600			127
Si		cf. supra				
In_2O_3/Si (inverse absorber)	vacuum evaporation	0.85/0.07				28
In_2O_3 doped with Sn	sputtering (intrinsic)	0.85/0.08 (120)				11, 113, 114, 128
HfC	intrinsic	0.65/0.1 (100)				17
LaB_6	intrinsic					115
SnO_2 doped with F	paint spray and bake (intrinsic)	0.92/0.14	200			11, 111, 129

TABLE I Continued

Material coating (/substrate)	Fabrication process	α/ϵ (temperature) (° C)	Thermal stability		Degradation mode	References
			Air (° C)	Vacuum (° C)		
F-doped SnO_2/black enamel	reactive spray	0.92/0.15	200			111, 116
MoO_3 doped Mo	intrinsic	0.95/0.1				11
Cd_2SnO_4	spray pyrolysis					130
Cd_2SnO_4/SiO_2	sputtering	0.8/0.1 (150)				131
Te/Al, Mo, Cu, Cr, Au	vacuum evaporation	0.9/0.03				132
Se/Al	vacuum evaporation	0.7/0.3				132
PbS	vacuum evaporation	0.98/0.2 (240) 0.3 (300)		300		85
PbS/Al	gas evaporation	0.93/0.21	120		oxidation (UV) of sulphide to sulphate	83, 84
PbS(+ SiO AR)/Al	vacuum evaporation	0.78/0.02 (100)				117, 118
PbS(+ SiO AR)/Ni	vacuum evaporation	0.86/0.04 (100)	240			117, 118
PbS(+ SiO AR)/Cr	vacuum evaporation	0.93/0.12 (100)	240			117, 118
PbS	paint (silicone binder)	0.94/0.8 (200)				85
PbS	paint	0.90/0.4 (100)				133
PbO_2/Cu	electrodeposition	0.98/0.3				134, 11
Cu_2S (BCu)	chemical conversion (intrinsic)	0.79/0.2 (200)				85
CuO_x (BCu)	chemical spray	0.93/0.11 (80)				5, 47, 63–67, 85
CuO_x/Cu (BCu)	chemical oxidation thermal oxidation	0.91/0.16 (100) /0.4 (200)				7, 68, 85
CuO (BCu)	selective etching of Al/Cu + thermal treatment	0.93/0.11				11
Cu	sputtering					135
Cu	sputter etching	0.92/0.1–0.3	$\leqslant$ 300	400	oxidation/diffusion	99
CuO/Au	paint	0.8/0.06				129
$CuO/Ag/Rh_2O_3$	paint	0.9/0.1				43
CuO_x + Fe + Mn	dip coating (paint)	0.92/0.13 (100)	> 150			129
CrO_x + Cu	paint	0.92/0.30 (100)				96
Cr_2O_3 + Co	plasma spray	0.90/0.5 (800)	800			85
$Cr–CrO_x/SiO_2$	sputtering	0.92/0.08 (120)	> 300			61, 136
Cr (CrO_x)	vacuum evaporation (+ oxidation)	0.8/0.15 (250)				96, 137
CrO_x–Cr (BCr)	electrodeposition	0.95/0.1 (100) 0.2 (200)	~ 250–300		oxidation/diffusion	44, 51–60

TABLE I Continued

Material coating (/substrate)	Fabrication process	α/ϵ (temperature) (° C)	Thermal stability		Degradation mode	References
			Air (° C)	Vacuum (° C)		
CrO_x–Cr (BCr)	electrodeposition	0.97/0.1	350			55, 138, 23, 71
CrO_x–Cr/Ni (BCr)	dipping	0.90/0.5				62
CrO_x–Cr/SS (BCr)	dipping	0.93/0.3	250			62
CoO_x (BCo)	electrodeposition + anodization	0.93/0.24 (260)				40
CoO_x(/Ni) (BCo)	electrodeposition + thermal treatment	0.95/0.1 (100)	300–450	300–450	morphological change	44–50
Co_3O_4 (BCo)	thermal oxidation	0.90/0.3 (140)	(1000?)			47, 85
CoS	electrodeposition	0.95/	300			44
WC + Co	plasma spray	0.95/0.28 (200) 0.4 (600)	> 800			85
WO_3/W	(CVD) + anodization	0.90/0.18	< 225			139
W (dendrites)	CVD	0.95/0.03	500			93, 140
WO_3/Ni	sputtering	0.83/0.07 (60)				141
Mo(+ AR)	CVD	0.82/0.08 (20)				125
Re (dendrites)	CVD					96
Ni (dendrites)	CVD	0.95/0.3 (100)– 0.6 (100)				94
Ni	sputter etching	0.92/0.09	< 300			99
Ni(NiO_x)	vacuum evaporation + thermal oxidation	0.8/0.1 (200)	300		further oxidation	97
Ni(NiO_x)	electrodeposition + anodization	0.95/0.3 (300)	< 350		further oxidation	7, 135
NiS–ZnS (BNi)	chemical conversion	0.9/0.1	200		sulphide conversion	36–38
NiS–ZnS (BNi) (single layer)	electrodeposition	0.88/0.1 (100)	220		sulphide conversion	85, 142
NiS–ZnS (BNi) (multi-layer coating)	electrodeposition	0.96/0.07 (100)	< 280		sulphide conversion	5, 26, 27, 39–43
NiC_x	reactive sputtering	0.8/0.03 (150)		$\geqslant 400$		72, 143
NiN_x	reactive sputtering					143
TiN_x	reactive sputtering	0.84/0.02 (127) 0.05 (327)	< 127	600		73
ZrN_x	reactive sputtering	0.86/0.02 (127) 0.04 (327)	< 127	600		73
ZrC_x	reactive sputtering	0.81–0.90/0.04 (127) 0.07 (327)	< 127	800		13, 73
ZrC_xN_y	reactive sputtering	0.88/0.03 (127) 0.05 (327)	< 127	800		73

TABLE I Continued

Material coating (/substrate)	Fabrication process	α/ϵ (temperature) (° C)	Thermal stability		Degradation mode	References
			Air (° C)	Vacuum (° C)		
ZrO_xN_y	reactive sputtering	0.90/0.05 (127) 0.08 (327)	< 127	800		73
Al_2O_3–ZrC_xN_y/Ag	reactive sputtering	0.91/0.05 (325)	175	700		129
CuC_x	reactive sputtering				diffusion	154
FeC_x	reactive sputtering	0.80/0.02 (150)		< 350		72, 144
SS–C_x + colloid film	reactive sputtering + dipping	0.95/0.05		⩾ 270		145
FeO_x/steel	chemical oxidation thermal oxidation	0.9/0.1 (100)	200			7, 35, 69, 70, 146
Fe–SiO_2/Cu	sputtering	0.90/0.04 (20)				147,
(Fe–Cr–Ni)O_x/SS	chemical or electro-chemical conversion	0.9/0.1				7, 74–75, 78, 85, 146, 148
(Fe–Cr–Ni)O_x/SS	thermal treatment	0.8/0.2				76, 77, 160
SS	sputter etching	0.93/0.22 (25) 0.24 (400)	⩽ 400	500		99
(Cr–Ni–Va)O_x	electrochemical co-deposition	0.94/0.40 (260)				49
Zn (ZnO)	anodization	0.8–0.9/0.1				7, 141, 146
Sn	chemical or electro-chemical conversion					7
Al (Al_2O_3)	anodization	0.8–0.9/0.35 (100)				85, 146
Al + Ni compound	thermal treatment	0.94/0.30				95, 98
Al + steel compound	thermal treatment	0.99/0.55				95, 98
Al + SS304 compound	thermal treatment	0.89/0.47				95, 98
Al + SS430 compound	thermal treatment	0.98/0.51				95, 98
Al_2O_3 + Ni composite	vacuum evaporation	0.94/0.10 (150) 0.35 (500)		500		21, 108, 110, 129
Al_2O_3 + Pt	sputtering	0.94/0.07 (150) 0.3 (500)		600		43, 110
Al_2O_3 + Au	sputtering	0.95/0.025 (20)		< 300		11
Al_2O_3 + Cu	sputtering	0.9/0.045 (20)		< 200		11
Al_2O_3 + Cr	sputtering	0.9/0.1				109
Al_2O_3 + Mo	sputtering	0.9/0.1				109
Al_2O_3 + Ag	vacuum evaporation	0.7/0.1				91
MgO + Au	sputtering	0.93/0.09 (20)	400	(300?)		43, 105–107

TABLE I Continued

Material coating (/substrate)	Fabrication process	α/ϵ (temperature) (° C)	Thermal stability		Degradation mode	References
			Air (° C)	Vacuum (° C)		
"Au-black"		/0.1	<300			6, 102, 103
"Au-smoke"	gas evaporation	0.99/0.1	100			43, 104
MgF_2 + Sn particles	vacuum evaporation	0.95/0.01				6
Al_2O_3–Mo–Al_2O_3/Mo	vacuum evaporation	0.94/0.08 (20)	450	600	diffusion	5, 34
InSb/Ag, Al	vacuum evaporation					11
(Fe, Mn, Cu)oxides	paint (silicone binder)	0.9/0.31 (100)	200			89
(Fe, Mn, Cu)oxides	paint (silicone epoxy)	0.9/0.31 (100)	200			89
(Fe, Mn, Cu)oxides + Al flake and silicone	paint	0.91–0.93/0.1 (20)	> 600			89
"Electroblack"	electrodeposition	0.86/0.05				11
"Maxorb"		0.97/0.10		150		43
"Solarox"	electrodeposition	0.92/0.20		200		43
"Solartex"	electrodeposition	0.95/0.16 (310)		700		43

Legend: AR: antireflection coating, SS: stainless steel, BCu: black copper, BCr: black chrome, BCo: black cobalt, BNi: black nickel.

TABLE II Summary of a few representative black paint or enamel coatings

Trade name	Manufacturer	Application	Type	α	ϵ (temperature) (° C)	Highest operating temperature (° C)	Durability indication
Pyromark 2800	Tempil	spray and bake	iron oxide + silicone	0.95	0.80 (315) 0.95 (871)	1371	refractory coating
Novamet 150	Ergenics	brush/spray no baking	inorganic pigment waterbase	0.96	0.84 (25)	815	good durability
Black Paint	Exxon		silicone + silicate base	0.98	0.9	> 700	
VHT Flameproof SP 102	Sperex	spray and bake	inorganic pigment + mod. silicone	0.82		650	
Heatproof Coating 8029	Cal Custom/Hawk	spray and bake	iron oxide + mod. silicone	0.95	0.83 (20)	649	
G-3113 HT Black	Ball	must be heat cured				649	
Inorganic Paint	Martin Marietta			0.9–0.95	0.9–0.95	> 550	

TABLE II Continued

Trade name	Manufacture	Application	Type	α	ϵ (temperature) (°C)	Highest operating temperature (°C)	Durability indication
S-31 Black Paint	Rockwell			0.8–0.85	0.8–0.85	> 550	
Thurmalox 270	Dampney	brush/spray heat cured	silicone base			537	
Pyromark 800	Tempil	spray and bake	silicone polyester base			427	
4279 Heat Resist Black	Rust–Oleum		carbon + silicone–alkyd.	0.95–0.96	0.87–0.90	427	good durability
G-3858 HT Black	Ball					315	
Stack Paint B68	Sherwin–Williams					260	
Syncryl Enamel	Mass and Wahlstein	brush/spray and bake	pigment + acrylic base			232	
37J-4 Paint	Mobil		gilsonite + oil			204	heat and moisture resistant black
719 Heat Resist	Gavlon	spray for steel	silicone acrylic base			204	
5779 Midnight Black	Rust–Oleum		carbon + acrylic emulsion	0.95–0.96	0.87–0.90	177	good durability
Durachem	Mass and Wahlstein	brush/spray and bake	epoxy base			177	good chemical resistance and weathering
Nextel Black Velvet	3M	brush/spray	carbon + SiO_2 (suspension of neoprene granules)	0.96–0.98	0.9 (25)	149	
Black Paint	Parsons			0.98	0.90 (130)	130	
412 Flat Black	Rust–Oleum		carbon + oil–alkyd base	0.95–0.96	0.87–0.90	121	good durability
436-3-8 Black Paint	Bostik			0.90	0.92		
Enersorb	De Soto			0.97	0.92		
7729 Black Paint	C.H. Hare			0.96	0.90–0.92		
Cr_2O_3 black enamel	–		Cr_2O_3 + ceramic frit	0.7		800	
Black Enamel	Ferro Corp.		black porcelain enamel	0.97–0.98			good durability
Duracron Super 600	PPG		organic black coating	0.97			
Solarsorb C-1077	Caldwell Chem.			0.9	0.6–0.8		

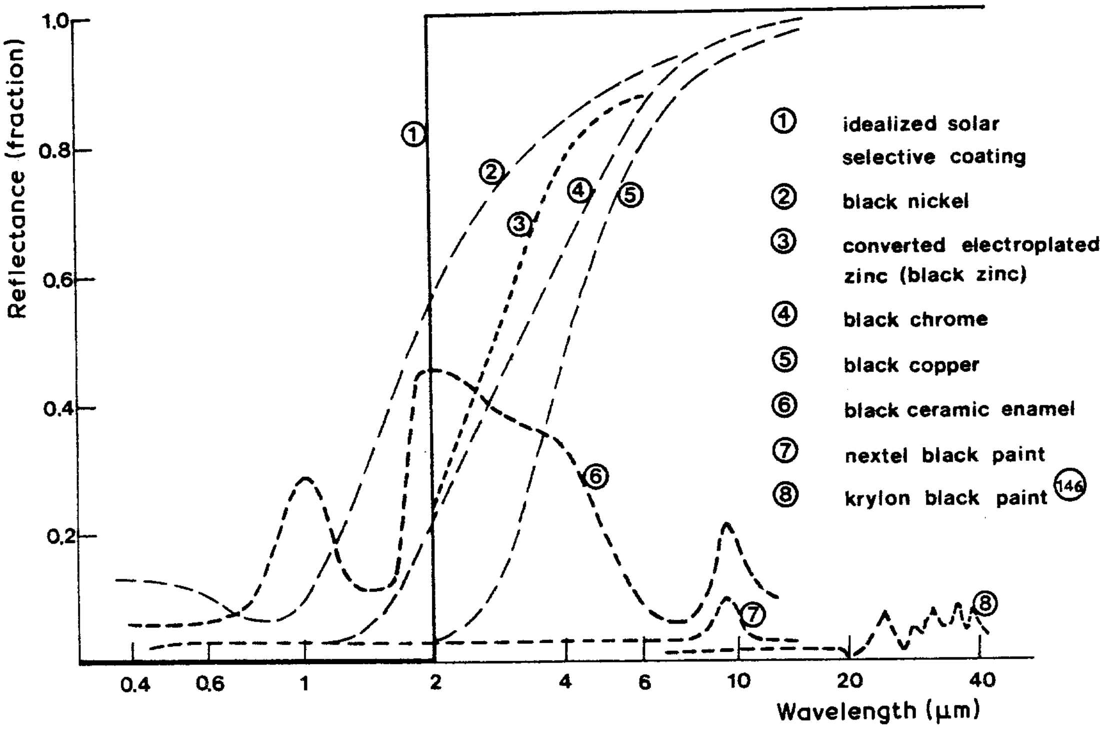


Figure 10 Typical reflectance curves of some common selective or non-selective coatings for solar collectors.

the infrared (radiation losses might, however, be reduced by IR-reflecting windows; cf. supra). The optical behaviour of non-selective coatings in comparison with some common selective surfaces is illustrated in Fig. 10. Infrared absorption peaks which may be noticed are due to inherent absorptions in the paint binder.

Because of the generally high emittance, the main selection criterion of non-selective paint coatings is high absorptance, good durability and low cost. Commonly, high temperature and heat resistant black paints are mainly used in industry as protective coatings for metals. In some cases specific colours 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. In view of their optical, adherence and durability properties, black automotive manifold paints and instrument blacks seem to be potentially good candidates for non-selective solar receiver coatings. Common pigments used to manufacture black paints are carbon black (0.02 to 0.1 μm), Fe_3O_4 (0.5 μm), amorphous graphite, bone black (325 mesh) and asphalt bases.

Degradation properties in terms of solar spectral response (absorption, emittance) with varying time or temperature, are little known. Temperature ratings, indcated in Table II, are mechanical adhesion ratings and are not to be viewed in terms of optical degradation. Optical degradation may take place at much lower temperatures.

Ceramic enamels have the advantage of high temperature and long-term durability and may be somewhat more solar selective than organic enamels or paint coatings. Nonglossy, "flat" ceramic enamels are, however, difficult to formulate and require firing at moderate to high furnace temperatures.

Chemical conversion coatings exhibit many potential advantages: the coating is fairly easily formed in a matter of minutes, the process is potentially inexpensive, many kinds of coatings are available for different substrate materials, such as steel (including galvanized and stainless steels), copper or aluminium, and some of the conversion systems even show moderate selectivity (Fig. 10). Chemical conversion consists of dipping a metallic surface into a strong oxidizer or sulphidizer which subsequently forms an oxide or sulphide coating on the metallic base. Usually, this surface is integral with the base metal, which is different from a painted or electrodeposited surface. The mechanical properties of the surface can though be quite different from those of the substrate. Drawbacks with most of the conversion coating baths are both temperature and safety. Many processes are run at 100 to 150° C and are very corrosive. Some of the available products, however, are safe enough to be applied by hand and can be used at room temperature. As an example, most conversion processes for zinc operate near room temperature. Zinc conversion may, on the other hand, be in question since in many circumstances zinc is known to form white corrosion products readily.

In Table III a summary of some potentially useful conversion systems, compiled from Lampert [146], is shown. Available durability data have been added.

4. Corrosion performance and durability data

Even though many promising coatings for photothermal energy conversion exist, very little is known yet about their performance 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. Similar statements have been made concerning water-side corrosion problems of solar collector panels [157, 158], although much more simplicity may be expected in this case.

4.1. Degradation mechanisms

Degradation of receiver surfaces principally occurs by loss of adhesion and deterioration of optical properties (decreasing absorptance, increasing emittance).

In considering causes of these degradation processes, one should generally distinguish between two different cases:

1. "inert" environments, such as in evacuated tube collector designs, in which problems will mainly be caused by elevated operational temperatures (including important temperature fluctuations and thermal shocks) and possibly the UV irradiation,
2. reactive environments, such as in most flat-plate collector designs, where moreover climatic conditions will have a significant or even determining effect on the durability of the exposed surface.

A pictorial representation of factors, governing the degradation and corrosion behaviour of solar receiver plates is shown in Fig. 11.

Degradation mechanisms in "inert" environments mainly comprise:

(a) interdiffusion between different layers or phases, which may cause a loss of absorptance and/or an increasing emittance,

(b) changes in surface morphology with loss of absorptance,

(c) differential thermal expansion of surface and substrate coating, which may lead to loss of adhesion and a subsequent decrease in the efficiency of thermal conductance or even a complete premature failure of the absorber plate.

(d) photo-induced physical or chemical processes [159] and general disintegration.

(e) reactions with residual atmospheres or outgassing products.

Electroplated coatings are mostly unsuitable for high temperature applications, since most electroplating baths have a number of organic and inorganic additives which become incorporated into the deposit and are subsequently able to diffuse into the coating along with the metal. This diffusion will be enhanced by a "rough" or "open" absorber coating structure. The same coating structure would normally also be most sensitive to chemical or corrosion attack.

Many of the coatings which have been developed for high operating temperatures are unsuitable for incompletely evacuated or oxidizing environments and will readily deteriorate in case of vacuum failure. Oxidizing environments will allow the conversion of metallic phases to oxides, which may reduce the absorptance of cermet or layer type absorbers. The presence of elevated temperatures and an oxidizing environment furthermore enhances diffusion of easily oxidizable metal components from the bulk layers to the surface and causes a growing oxide thickness with a probable increase of the IR emittance. Oxygen may also diffuse into the coating and react internally.

Degradation at elevated temperatures may be minimized by choosing refractory metals or compounds for the absorber layer and using refractory materials or special diffusion barriers for the underlayer.

Degradation in common climatic, reactive environments may however be much more complex and may moreover be due to a variety of:

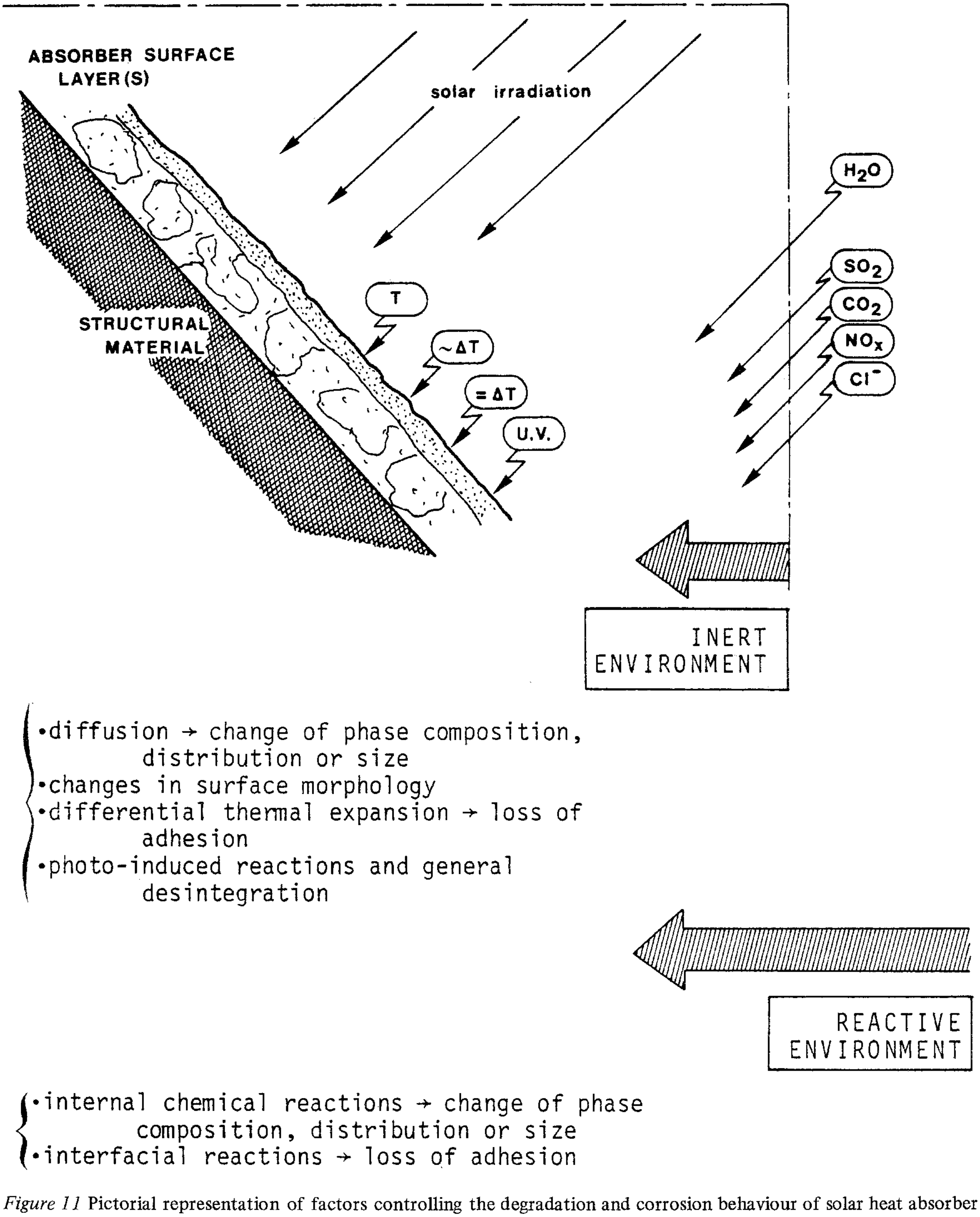
(a) internal chemical or electrochemical reactions in a surface layer, which cause disintegration or changes of phase composition, distribution or size (loss of absorptance and/or increasing emittance), and

TABLE III Summary of some potentially useful chemical conversion systems

Trade name	Manufacturer	Type	α	ϵ (temperature) (° C)	Deposit characteristics	Corrosion resistance
Key Kote 70 Blackening Agent	Allied-Kelite	Zinc phosphate for ferrous metals				
–	Allied-Kelite	Molybdenum dipping process for zinc coatings	0.88	0.14		poor corrosion protection (zinc corrodes) [151]
–	Allied-Kelite	Chromate dipping process for zinc coatings	0.91–0.93	0.18–0.28		good corrosion resistance [151]
Presto Black	Birchwood Casey	Non-caustic cold conversion solution for ferrous metals				
Aluma Black	Birchwood Casey	Non-caustic cold conversion solution for aluminium	0.96–0.97	0.55–0.73 (100)		poor corrosion resistance (white corrosion products); organic sealant needed [152]
Antique Black	Birchwood Casey	Cold Conversion for copper				
Zinc Black	Birchwood Casey	Cold Conversion for zinc				
Kenvert ZB	Conversion Chemical Corp.	Oxidizer for zinc				
Kenvert 311	Conversion Chemical Corp.	Oxidizer for zinc				
Du-Lite Black	Du-Lite Chemicals	Chemical finish for steel				
Du-Lite 3-0	Du-Lite Chemicals	Chemical finish for stainless steel				
Du-Lite Cu Black	Du-Lite Chemicals	Copper oxidizer				
Ultrex Z-27	Enequist Corp.	Acidic solution for zinc				
Ebonol S	Enthone	Caustic oxidizer for steel	0.89	0.07	Fe-oxide 1–5 μm thick	poor rust resistance; improved resistance using organic overcoats, but organics unstable above 200° C? [35]
Ebonol C	Enthone	Caustic oxidizer for copper	0.84–0.95	0.06–0.40	CuO 1.3–5 μm thick; stable to 204° C	★degrad. after 500 h at 30° C and 100% RH; ★no visually observed corrosion products after 2.5 years in marine atmosphere [153]
Ebonol Z	Enthone	mild alkalizer for zinc	0.75	0.13	metal oxide 1–2.5 μm thick; stable to 170° C	
Ebonol SS-48	Enthone	Oxidizer for stainless steel			oxide/sulphide 1.5–2.5 μm thick	
Enthox ZB-992	Enthone	Acidic strong oxidizer			chromate conversion	good durability [154]
Nickel Penetrate	Heatbath Corp.	Steel alkaline oxidizer with nickel			Fe_3O_4 2.5 μm thick	
–	Permaloy	Anodizing of Al	0.94	> 0.4 (0.71)		risk of fading of the dyes used [155]

TABLE III Continued

Trade name	Manufacturer	Type	α	ϵ (temperature) (° C)	Deposit characteristics	Corrosion resistance
–	Int. Nickel	Immersion of stainless steel in acid solutions			coloured surface films:	
			0.92	0.14	"blue"	
			0.90	0.18	"black"	
			(cf. [156])			
Permablack	A.F. Holden Co.	For ferrous metals			black oxide	
Lustre Black	A.F. Holden Co.	For ferrous metals			Fe-oxide film	
Roblack Zn	R.O. Hull Co.	Mild acid oxidizer for zinc				Mild corrosion protection
Roblack Fe	R.O. Hull Co.	Strong alkali oxidizer for steel			Fe-oxide 0.25 μm	
Roblack Cu	R.O. Hull Co.	Strong alkali oxidizer for copper			Cu-oxide; etching needed for dull surface	Corrosion resistant
IRCO Blackjack	R.O. Hull Co.	Acid conversion for steel			Matt black	
Electroless Black Magic	Mitchell–Bradford	Alkaline oxidizer for aluminium	0.82	0.12		
Ferrotone	Turco Product	Alkaline oxidizer for steel				
Optical black	Martin Marietta	Anodized Al coating				
–	Alcoa	Alkaline conversion	0.93	0.35		
–	Climax Moly	425° C bath; dichromate conversion dip for stainless steel	0.80	0.02–0.6		



- diffusion → change of phase composition, distribution or size
- changes in surface morphology
- differential thermal expansion → loss of adhesion
- photo-induced reactions and general desintegration

- internal chemical reactions → change of phase composition, distribution or size
- interfacial reactions → loss of adhesion

Figure 11 Pictorial representation of factors controlling the degradation and corrosion behaviour of solar heat absorber plates.

(b) interfacial corrosion reactions, which bring about loss of adhesion of the surface coating. Environmental or climatic factors that could play an important role include:

1. The presence of chlorides (coastal regions), sulphur dioxide (industrial and urban areas), or other atmospheric pollutants.

2. The presence of high humidity in the atmosphere. Atmospheric corrosion becomes significant when the relative humidity in the atmosphere exceeds approximately 70%. Where hygroscopic contaminants are deposited on a metal surface, the critical relative humidity for corrosion may be lowered from 70% to a value as low as 50%.

3. The high energy ultraviolet component of the sun's rays plays an important role in the breakdown of organic materials, whether these be paint coatings, mastics, rubbers or bulk plastics. This could affect the durability of many components in the solar heater, including the black heat absorbing collector surface, especially when it contains organic or semiconductor [159] components. UV irradiation can lead to oxygen depletion of lattice surface sites, diffusion and induced bound-state defects or to breakdown of organic molecules. This can result in colour changes and an increase in the imaginary part (the extinction coefficient) of the refractive index of the material. Another example is the photo-oxidative conversion of selective metal sulphides to sulphates.

4. Diurnal temperature fluctuations are often considerable. This can lead to appreciable condensation of moisture onto a cool metallic surface at night. The length of time of water retention on the surfaces has an important effect on subsequent corrosion problems. Temperature fluctuations, together with moisture condensate, are detrimental both to metals and to coatings on the metallic substrate. Moisture penetration, especially through thin semiconductor layers, may be expected to accelerate degradation of the underlying substrate and to induce a quick deterioration of the absorber surface by corrosion.

5. A further complication of temperature fluctuations is that differential expansion of the various materials involved could set up stress conditions which can result in cracking or loss of adhesion of the coating from its substrate. This will particularly be meaningful in the case of thermal shocks or during summer stagnation periods where very high temperatures can be reached. Stress cracking of the surface layer opens the way for subsequent attack or further oxidation of the substrate. All these alterations of surface or subsurface structure will cause changes of optical properties.

In minimizing degradation under the present circumstances, electrochemical as well as mechanical compatibility of the coating and the substrate is a prime requirement. The use of dissimilar metals such as a zinc absorber and a copper substrate can allow the possibility of localized galvanic corrosion and loss of surface integrity. Cracks due to differential thermal expansions in the surface of, for instance, a copper oxide-on-copper selective tandem will expose the substrate to further oxidation or corrosion attack [162].

Taking the previous rule into account, the main weapon in combating corrosion in reactive environments is the correct choice of the absorbing layer material and the use of a corrosion resistant structural substrate or at least a corrosion resistant interface-layer between the structural metal and the receiver coating (cf. Fig. 3). Unfortunately, readily accessible data about the corrosion behaviour of different receiver systems remain scarce at the present time.

4.2. Experimental data

4.2.1. Temperature stability

Whereas temperatures in flat-plate non-selective absorber systems are generally limited to about 150° C, maximum (stagnation) temperatures in solar selective receiver systems reach 200° C, or may be much higher in concentrating collector designs. Solar absorber surface coatings have been developed for operation over an extensive range of temperatures. Available temperature stability data have already been indicated in Tables I to III. Except for non-selective and for some moderately selective receiver surfaces, electrodeposited black chrome has appeared as the most popular and successful of a variety of coatings produced by electrodeposition and chemical conversion techniques for operation in flat-plate collectors up to 200° C. Thermal stability of black chrome has been investigated by a number of authors [13, 23, 71, 163–168]. Sputtered metal carbides or cermets and silicon-stabilized multi-layers fabricated by chemical vapour deposition [42, 169] have been developed for operation in concentrating system with surface temperatures up to 700° C. Diffusion problems have for instance also been overcome in the AMA multilayer absorber [5, 34], which shows a quite satisfactory high temperature behaviour. For temperatures in excess of 700° C, which are experienced in central receiver systems, refractory non-selective paints and oxidized stainless steel coatings have been used [43].

4.2.2. Corrosion and weatherability properties

Obviously, no general rules can be formulated about corrosion and weatherability properties of the different proprietary black paint systems which may be used for non-selective solar absorbers. For a specific system one is usually dependent upon the manufacturer's product literature, which is not always available and which will mostly be limited to results of some standard qualification tests (e.g. Salt Spray Test, SO_2 exposure, adhesion tests etc). It can, however, be expected that the results of these tests, if available, in many cases may not be interpreted as a measure for weatherability or ageing behaviour of the product, especially not in specific solar collector environments. Detailed literature data about the weatherability behaviour of some specific paint system under these circumstances do not seem to be available. Some qualitative statements are represented in Table II. In general, the most obvious degradation mode is loss of adhesion of the coating. Loss of adhesion is generally due to poor initial adhesion or to interfacial corrosion. Locally initiated corrosion processes will lead to blistering, filiform corrosion and complete degradation of the coating surrounding the corrosion-initiation region. Interfacial corrosion will be minimized to some degree by choosing corrosion resistant baselayer materials. So, poor corrosion resistance may for instance be observed with common carbon steels or galvanized steels, whilst satisfactory resistance is experienced with the same coating applied on a nickel or stainless steel substrate, provided a sufficient initial adhesion and compatibility can be obtained. Poor initial adhesion will, on the other hand, highly depend upon a correct pretreatment of the metal surface, and the use of a specific primer may be required.

In general, no such complications are observed with conversion coating systems, in which surface coating and substrate form an integrity. Qualitative corrosion resistance data for a number of proprietary black conversion coatings are available. They have been summarized in Table III.

As opposed to different non-selective paints or conversion coatings, many selective absorber surfaces cannot provide sufficient corrosion protection of the solar receiver system on their own. Because a selective surface is a surface – and is formed by producing an extremely thin coating on a metal base – this coating normally cannot offer any substantial corrosion protection to the base. Thus the base itself must be stable to the effects of atmospheric corrosion and oxidation. This means that the choice of the substrate materials will be of prime importance in the case of most selective absorbers.

Porous semiconductor surfaces on copper, aluminium or steel have been cited to be particularly troublesome in humid atmospheres, but enhanced durability was expected if a nickel coating was used beneath the semiconductor film [170].

The same results have been experienced with black chrome selective coatings, which generally exhibit an excellent humidity resistance, but which nevertheless provide inferior results if directly applied on bare or galvanized steel, aluminium or copper, in comparison with substrates such as nickel or stainless steels [17, 162, 172]. Black chrome surfaces on bare steel were found to rust, while the humidity resistance of black chrome on galvanized steel was cited to be poor [35]. Resistance could, however, be improved by combining the so-called 'Solarchrome' process (prop.of Corillium Corp.) with a suitable propriety pretreatment of the base steel surface [173], or by using an organic overcoat. The use of organic overcoats to increase the moisture resistance has recently been discussed by Reiss [174]. Good humidity resistance, on the other hand, was also observed if a nickel base was applied on iron samples (provided it has a minimum thickness of $12\,\mu$m) [175], and extraordinary durability was claimed for black chrome on stainless steel substrates (even on relatively less expensive 18Cr–2Mo ferritic steels) [62, 176]. On the effect of atmospheric contaminants, only meagre information is available, although no deterioration was found after 1200 h of salt spray testing of black chrome coatings applied on Ni-plated steel or copper [55].

Nickel black coatings, on the contrary, are generally observed to be less stable and less resistant to moisture, especially at higher temperatures [5, 7, 35, 88, 177, 178]. Experiments have been performed in which the black was washed away after only 24 h humidity testing, even if the coating was applied on a nickel base [35]. Accelerated humidity tests on black nickel applied on galvanized iron, zinc electroplated aluminium or zincated aluminium showed a deleterious effect on α and ϵ parameters (Table IV) [37] while stagnation tests in natural environments on black nickel with a zinc plated mild steel substrate revealed some discolouration and visible corrosion after only 3 months of exposure. One year of stagnation in a humid tropical area of black nickel on galvanized iron gave a doubling of the infrared emittance ($0.2 \rightarrow 0.4$) [36]. Recently, however, polymer coatings which are highly transparent in the

TABLE IV Change of α and ϵ for black nickel on different substrates after increasing times of accelerated humidity testing (MIL-STD-810B, Meth. 507, proc. 1) [37]

	Galvanized iron		Zinc electroplated aluminium		Zincated aluminium	
	α	ϵ	α	ϵ	α	ϵ
0 days	0.93	0.08	0.94	0.1	0.90	0.14
2 days	0.90	0.14	0.91	0.17	0.85	0.2
4 days	0.82	0.2	0.80	0.23	0.82	0.27

infrared have been developed for use on black nickel surfaces. They seem to be able to provide long-term stability under severe corrosion test conditions [174]. Increased humidity resistance of black nickel coatings has also been claimed by Kumar *et al.* [38] for their electroless surfaces since their coatings almost contained no sulphides. This would impede strong humidity degradation processes wherein the sulphides are converted into hydroxides and oxides, with corresponding loss in optical properties. Experimental proof, however, was not provided. Years of experience with black nickel selective absorbers in Israel, on the other hand, show that these surfaces can be durable. This discrepancy between everyday practical experience and many laboratory results might be partly explained by particular climatic conditions, but may also be interpreted as a lack of reliability or convertability of many test results or methods. More research in this field seems to be necessary.

Also copper oxide on copper coatings have proven that they can be durable in practical service (Australia). Selectivity of the coating might however diminish, due to patination of the surface under influence of moisture [7, 172], or because of further oxidation of the metal substrate (increasing ϵ) [162]. The latter also explains the unsuitability of this type of coating for elevated temperatures [7, 177].

Chemically oxidized stainless steel or anodized aluminium (only moderately selective) seem to suffer less from decreasing absorptance or increasing emittance values as a function of time [162].

Excellent durability properties may also be expected for some other wavefront-discriminating surfaces, such as dendritic tungsten, or might be achieved with absorbing surfaces such as black molybdenum or ceramic enamels.

Table V summarizes generally the overall durability of some common coatings for solar heat collectors.

TABLE V Durability of coatings for solar heat collectors

Coating	Durability
Black Paint	No general rules – depending upon type of paint and substrate material.
Organic Enamel	Limited stability at high temperature.
Ceramic Enamel	Extremely stable.
Black Chrome	Stable.
Black Nickel	May be destroyed by moisture.
Black Copper	Patinates with moisture; limited stability at elevated temperatures (grows in thickness with temperature).
Black Zinc	Not completely defined – probably not very successful (white corrosion products)

5. Conclusions

From the results of an extensive literature search concerning absorber surfaces for photothermal solar energy conversion and their durability, the following conclusions appear to be most significant.

1. Many promising coatings for enhanced photothermal energy collection exist and a lot of them can in principle be applied onto a variety of structural absorber plate materials, such as bare or galvanized carbon steel, copper or aluminium. Durability problems, however, often demand for a more corrosion resistant substrate, such as a base nickel layer or stainless steel.

2. Selective absorber surfaces potentially offer the best optical and thermal performance, but with their exacting optical properties they can be expected to be most sensitive to degradation. Some promising cost-effective coatings for low temperature use (< 150 to $250°$ C) are copper oxide formed by chemical conversion, black nickel and black chrome. Although stability is greatly influenced by the corrosion resistance of the substrate metal, the latter coating appears to be the most stable but will probably be matched in durability (and maybe cost) by, for instance, chemically or electrochemically converted stainless steel surfaces. To date the former systems are however favoured because the capital equipment already exists and several of the proprietary processes have been used for years, although not necessarily for solar energy applications. For higher temperatures diffusion and/or oxidation processes will cause severe problems. Some systems in which these have been overcome are, for instance, the multilayer AMA coating, stabilized silicon absorbers, tungsten dendrites and a number of cermets. Most of these systems, however,

need a careful tuning of production parameters and are only vacuum-compatible. Cost-effectiveness will at least require concentrating collector designs.

3. Several types of coatings and surface preparations, other than selective absorbers, can be utilized for economical collection of solar energy, especially for low-temperature applications such as flat plate solar collectors. This group of non-selective or moderately selective coatings consists of matt black paints, ceramic or organic enamels and certain chemical metal conversion coatings. Ceramic enamels have the advantage of high temperature and long-term durability and painted or chemical conversion coatings are very attractive because so many potential processes exist, they are fairly easy and inexpensive to apply and a variety of substrate materials may be used. The equipment to apply these coatings already exists and the coatings are currently used for many commercial items. The coatings even have a potential to be selective by coating them with an IR-reflecting window material or by embedding semiconductor particles (e.g. PbS), in which case the painted coatings need a binder that 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 to 200° C). The conversion coatings need to be optimized and formed in such a way that they exhibit poor infrared emittance.

Energy losses of the present absorber system can also be reduced by making the cover window of the collector box IR-reflective in order to achieve a similar low effective emittance.

4. All of the previous coatings need to be evaluated in terms of stability and lifetime. Until the durability and expected life of a solar heating system are determined, decisions on cost effectiveness, savings etc. are meaningless.

Efficient, economic design and operation of a solar collector is a trade-off between a set of materials which possess favourable optical and thermal properties and a choice of compatible materials which can be relied upon to provide a relatively long, trouble-free lifetime involving a minimum of maintenance. In these durability considerations, absorber surfaces play a determining role. If the receiver surface degrades, so does the entire system.

5. Evaluation of durability and lifetime of the absorber coating has to be carried out in circumstances which involve temperature cycling and (a simulation of) actual collector environments. These environments can be very harsh. In "inert" environments, such as in evacuated tube collector designs, problems will mainly be caused by elevated temperatures (including important temperature fluctuations and thermal shocks) and possibly the UV irradiation. In reactive environments, such as in most flat-plate collector designs, moreover, climatic conditions will have a significant or even determining effect on the durability of the exposed surface. Coastal sites expose the coating to sea air and salt, industrial and urban localities can produce atmospheres with above average levels of sulphur dioxide, chlorine, nitrous oxide and more toxic effluents and contaminants. Moreover, wetting of the absorber surfaces, due to diurnal temperature fluctuations with condensation at night, might lead to an important increase of the corrosivity of the local environment.

6. At the present time, only a minute amount of useful durability data (i.e. which would allow an informed evaluation of the relative trade-off between production costs and predicted lifetime) exist. Some very basic testing needs still to be done to determine humidity and corrosion or degradation resistance. A full-scale durability and materials evaluation programme is highly demanding. Not only should efforts be directed towards producing a quantity of durability data in in-service conditions, but attempts should be taken to identify basic causes of degradation in order to facilitate product improvements or the outlining of protective measures. If possible, the effect of individual environmental parameters should be quantified, together with their synergetic action. Therefore it is necessary to develop suitable accelerated tests and to establish the correlation with in-service conditions.

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