

Selective Coatings on Flat-plate Solar Collectors

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ABSTRACT

Solar radiation can be effectively trapped by using selective coatings because the solar range of wavelengths and the thermal range of wavelengths generally do not overlap, and thus the performance of solar collecting devices can be improved. Several selective surfaces such as black nickel, black chrome, copper oxide, lead sulphide, etc., have been developed and deposited either on copper, aluminium or on galvanised iron sheet, and their spectral reflectance properties have been studied by several workers in different countries. The results of these studies are reviewed in this paper. The theoretical efficiency obtainable from these selective absorbers is calculated with the help of an improved expression and the results are compared with a non-selective absorber. It is shown that for solar water heaters for medium temperature heating (up to 60-70°C) there is not much advantage in using a selective coating. This advantage increases as the collection temperature increases.

INTRODUCTION

Tabor (1) and Gier and Dunkle (2) were the first to demonstrate the principal and the benefits derived by using selective coatings on solar collectors. Since 1955, there has been considerable development in the selective coatings which have applicability to solar collectors, and a number of mechanisms for producing the desired combination of properties have been evolved. Among the most important are those by Irvine et al. (3) Gillette (4), Salem et al. (5), Williams et al. (6), Edwards et al. (7), Tabor (8), Tabor et al. (9), Martin and Bell (10), Schmidt et al. (11), Close (12), Hottel and Unger (13), Kokoropoulos et al. (14), McDonald (15), Driver et al. (16), Lincoln et al. (17), Power et al. (18), Gogna et al. (19), Harding (20), Cathro et al. (21), Cathro (22) Pettit and Sowell (23), Vanderleij (24), and Wright and Mason (25).

The spectral distribution of solar radiation is similar to the black body radiation at a temperature of about 6000 K with a peak intensity at about 0.5 μm . The solar radiation is entirely confined to the range of wavelengths 0.3 to 2.4 μm , while a terrestrial body heated to a temperature of 273 K emits radiation with a peak wavelength of 7.8 μm and there is no radiation below 3.1 μm . Thus the spectrum of solar radiation and that of bodies heated to moderate temperatures do not overlap, and hence surfaces can be developed which are highly absorbing in the solar range of wavelengths, i.e. 0.3 to 0.4 μm , and highly reflecting (low emitting) in the thermal range of wavelengths. There are the following surfaces:

Type	Properties		
	Absorptance	Emittance	Example
First	High	High	Ordinary black paint
Second	High	Low	Black nickel, Black chrome
Third	Low	High	White paint
Fourth	Low	Low	Aluminium foil

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For solar energy application, we are interested in the second type of surface which is known as a selective surface. Fig. 1 depicts the spectral reflectance of an ideal solar selective surface.

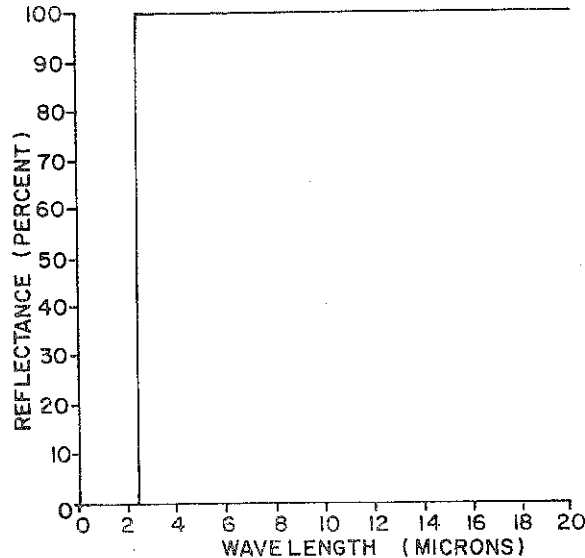


Fig 1. Spectral reflectance of ideal solar selective surface

A high conductivity surface has a low thermal emittance; the base for any low emittance surface is usually metallic. The selective surface on a metallic base can be obtained by

1. Applying a thin light-absorbing infra-red transmitting coating to the base.
2. Chemically-converting the metallic base into a compound having properties of coating like 1 above.
3. Adjusting the topology of the surface to provide different optical properties for short wave and long wave thermal radiation.

1. Deposited Coatings

Most of the currently used selective coatings are of the first type in which a single layer or multiple layers of nickel black or chrome black are electrodeposited on nickel, zinc, galvanized iron, tin or copper substrates. Weingartner (26) has deposited interference coatings in vacuum. Deposition by sputtering has also been proposed by Thorton (27). Electrodeposition of lead oxide has also been proposed by Bowen and Schmidt (28).

Thin layers of a semiconductor such as silicon can be deposited by chemical vapour deposition techniques. As silicon is transparent in the infra red, it has no effect on the emissivity of the base on which it has been deposited. However, due to its high refractive index there is a considerable reflection in the solar spectrum; therefore, it has a low solar absorptance.

Escoffery and Luft (29) have suggested that absorptance can be improved by using heavily boron doped silicon. Another method of increasing absorptance, by applying an antireflecting coating of several layers to build up an interference stack, has been proposed

by Wells et al. (30). One limitation of this method is that the hot silicon vapour will react with the base material, i.e. aluminium.

In multiple layers, coatings generally used are black nickel (NiS/ZnS) (9) and dielectric-metallic-dielectric coatings (10). In this process alternate layers of dielectric and metal are deposited in quarter wavelength films for the solar range of wavelengths. A three layer coating of SiO_2 -Al- SiO_2 on aluminium (10) is a good example of this type of selective coating. A third type of coating is the dielectric-dielectric-dielectric coating (11), which is also a multiple layer interference coating.

Thin coatings of selective paints or particulate coatings (6) are also gaining importance. The paint is made from an IR transparent semiconductor, e.g. lead sulphide (6) and microspheroid carbon particles (31), in a fine powder form and preferably including a high void ratio to reduce the effective refractive index and hence the surface reflectivity, mixed in a binder. It is then sprayed as a thin layer on the metal base. The binder results in higher emittance values than for the other processes.

2. Conversion coatings

The most commonly used coating in this group is copper oxide on copper first described in 1955 and used extensively in the Australian collector industry. High temperature and corrosion stability are its limitation and under high humidity this coating deteriorates.

Zinc has also been blackened chemically by Horner and Green (32) and it is an alternative to the nickel black on zinc process.

Nickel may also be blackened by conversion processes but optical properties are generally poorer than those obtained by the electrodeposition technique. Iron can also be converted into a selective absorber by heating or chemical conversion. The Ebonol process produces good stability but poor solar absorptance; therefore it is of little use.

By controlled oxidation at high temperature, stainless steel can be made moderately selective. Chemical colouring of stainless steel is also possible for getting selective coatings on it, but the high cost of stainless steel would not be desirable for use in the fabrication of solar collectors.

Williams (33) has proposed a method of chemical conversion of aluminium but the thermal emittance is very poor $\epsilon = 0.35$ and $\alpha = 0.93$.

Wright and Mason (25) have developed a novel selective coating which is commercially available as "Maxorb". In this type nickel foil is blackened into black nickel oxide dielectric layers. It has absorptivity as high as 0.98 due to its surface morphology, which consists of a dielectric type structure; its emissivity is as low as 0.09. This foil can be stuck to any flat-plate solar collector. This type of coating has an edge over other coatings because the continuous production of the black selective surface results in a significant cost reduction over a batch type process, and a much higher standard of quality control. The flexibility of the system enables the foil to be applied directly to any substrate, steel, aluminium, copper, etc.

3. Topological coatings

Partially selective coated metal substrate properties can be improved by simply V grooving the surface. In this case because of the multireflection of incident solar radiation the total

absorptance is increased and the emittance is also slightly increased. For example, a surface having absorptance 0.6 and emittance 0.05 on a flat normal collector will give an effective absorptance of 0.90 and emittance 0.10 with 55 degree grooves. The multiple reflections in a V grooved surface with various angles of incidence are shown in Fig. 2.

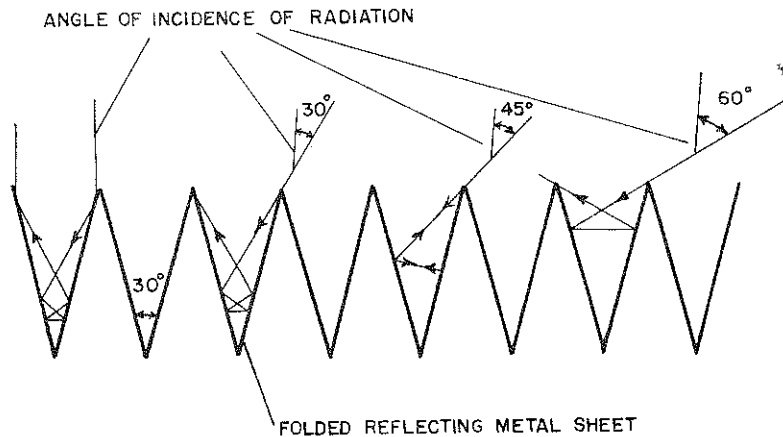


Fig. 2. Absorption of solar radiation by successive reflections on folded metal sheets

As similar effect is obtained by creating a dendritic surface structure on a metal surface with the cavities in the micron size, which will result in high absorption of visible light and very little effect on the basic emittance of the metal. Dendritic tungsten (34) is a good example of this process.

As tungsten dendrites are costly, now Ni dendrites are being produced by CVD. Horwitz (35) has proposed an approach in which the topology is made by providing very small holes or meshes that distinguish between optical and thermal wavelengths. High ratios are predicted theoretically, but practical surfaces have not yet been obtained.

SELECTIVE STRUCTURES

The effective emittance E_e of one surface having emittance E_1 in proximity with another surface having emittance E_2 is given by

$$E_e = 1 / (1/E_1 + 1/E_2 - 1) \quad \dots \dots (1)$$

Thus a high infrared reflecting coating on the underside of the cover glass of a flat-plate collector will be just as effective as a selective absorber. It has the advantage that it does not have to tolerate very high temperatures. Conductivity layers on glass that are reasonably transparent have been known for many years. Thin layers of gold (deposited in vacuum) have been used as conducting layers but transmission is poor. Layers of tin-oxide doped with antimony, or indium oxide doped with tin, are more usual.

These layers are deposited by CVD techniques. The heat mirror coating developed by Weingartner (36) is an alternative to selective coatings on the absorber surface. Solar traps and opaque and transparent wall honeycombs are also other selective structures being used.

THE EFFECT OF A SELECTIVE COATING ON THE EFFICIENCY OF A COLLECTOR

In a flat-plate collector heat losses with either nonselective or selective coatings are given (in terms of the nomenclature listed below) by Klein (37):

$$U_L = \frac{Q_r + Q_c + Q_B + Q_E}{A (T_p - T_a)} \tag{2}$$

Where Q_r and Q_c are the instantaneous rates of energy transfer to the transparent cover above the absorber plate by the processes of radiation and convection respectively; Q_B is the instantaneous rate of energy conduction through the insulation below the plate; Q_E is the instantaneous rate of energy loss from the plate due to edge effects. Here

$$Q_r = \frac{\sigma A (T_p^4 - T_a^4)}{1/ [\epsilon_p + 0.05N (1 - \epsilon_p)] + (2N + f - 1)/\epsilon_g - N} \tag{3}$$

and

$$Q_c = \frac{A(T_p - T_a)}{(NT_p/C)/[(T_p - T_a)/(N + f)]^{0.33} + 1/h_w} \tag{4}$$

where

$$f = (1 - 0.04h_w + 0.005h_w^2) (1 + 0.091 N), \tag{5}$$

$$C = 365.9 (1 - 0.00883 B + 0.00012989 B^2), \tag{6}$$

where B is tilt of the collector, and h_w is the convection coefficient between the top glass cover and the ambient air. This convection coefficient is a function of wind speed. McAdams (38) recommends

$$h_w = 5.7 + 3.8 W \text{ Wm}^{-2} \text{ K}^{-1}. \tag{7}$$

The above relations are applicable for the following conditions:

$$320 \text{ K} \leq T_p \leq 420 \text{ K},$$

$$260 \text{ K} \leq T_a \leq 310 \text{ K},$$

$$0.1 \leq \epsilon_p \leq 0.95, \tag{8}$$

$$0 \leq W \leq 10 \text{ m s}^{-1},$$

$$1 \leq N \leq 3,$$

$$0 \leq B \leq 90^\circ.$$

Also

$$Q_B = A (T_p - T_a) / (\delta/k + 1/h_b). \tag{9}$$

Tabor (39) recommends

$$h_b = 12.5 \text{ to } 25.2 \text{ Wm}^{-2} \text{ K}^{-1}. \tag{10}$$

Whillier (40) treated edge losses as

$$Q_E = h_e A_p (T_p - T_a), \tag{11}$$

where

$$h_e = 0.6 \text{ Wm}^{-2} \text{ K}^{-1}. \tag{12}$$

The collection efficiency of the collector is given as

$$\eta = \alpha\tau - (Q_r + Q_c + Q_B + Q_E)/AH. \quad \dots\dots (13)$$

Here

- A = Area of the collector plate surface, m^2
- A_p = Perimeter area of the collector, m^2
- h_b = Convection coefficient between the bottom of the insulation and the environment, $Wm^{-2}K^{-1}$
- N = Number of glass covers
- B = Tilt of collector measured from horizontal, degrees
- α = Absorptivity of the coating
- τ = Transmittance of the cover
- H = Instantaneous solar radiation on the collector, Wm^{-2}
- T_a = Ambient temperature, K
- T_p = Mean plate temperature, K
- W = Wind speed, ms^{-1}
- U_L = Collector overall energy loss coefficient, $Wm^{-2}K^{-1}$
- ϵ_g = Thermal emissivity of glass
- ϵ_p = Thermal emissivity of the plate surface
- k = Thermal conductivity of the insulation, $Wm^{-1}K^{-1}$
- σ = Stefan-Boltzmann constant, $Wm^{-2}K^{-4}$
- δ = Thickness of the bottom insulation, m

Fig. 3 illustrates the relation between calculated efficiency as a function of absorber temperature with different values of solar absorptance and thermal emittance of the coatings. These calculations are made for single as well as for double glass covers.

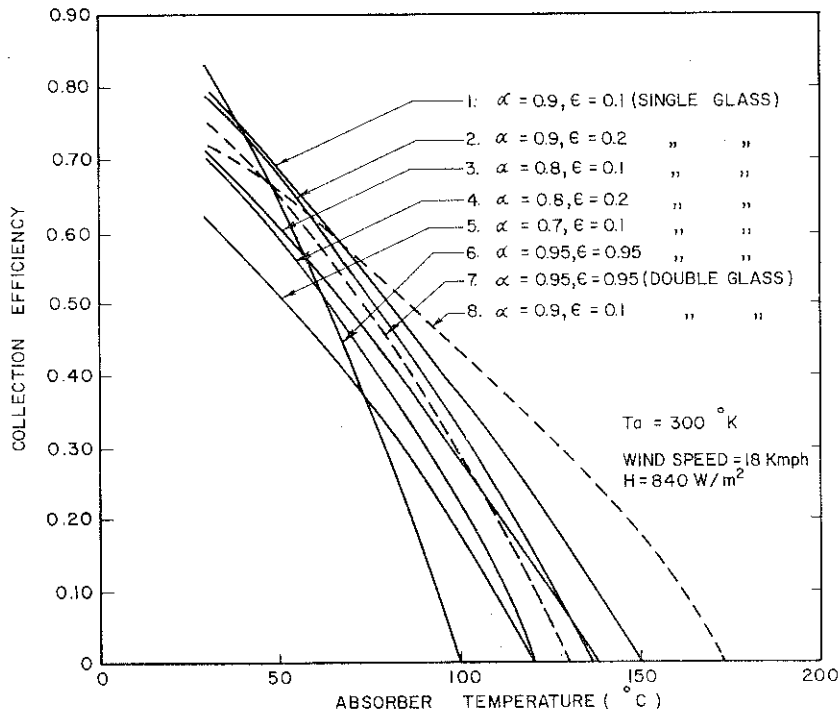


Fig. 3. Effect of selective coating on collection efficiency at different absorber temperatures

It is seen that at sufficiently low temperatures, up to 50°C, nonselective coatings are superior to selective coatings with $\alpha = 0.8$ and $\varepsilon = 0.1$, $\alpha = 0.8$ and $\varepsilon = 0.2$, $\alpha = 0.7$ and $\varepsilon = 0.2$, and are just equivalent to a selective coating with $\alpha = 0.9$ and $\varepsilon = 0.1$. Also at this temperature the performance with a single glass is better than with a double glass cover. Therefore, for low temperature application a nonselective coating is preferable.

It is also concluded from these curves that absorptivity plays an important role. One should not go to low emissivity at the cost of reduction in absorptivity. Fig. 3 shows that coatings having $\alpha = 0.9$ and $\varepsilon = 0.2$ are superior to those with $\alpha = 0.8$ and $\varepsilon = 0.1$. Also coatings having $\alpha = 0.8$ and $\varepsilon = 0.2$ are superior to those with $\alpha = 0.7$ and $\varepsilon = 0.1$. Thus absorptivity should not be reduced considerably. It is also seen that with nonselective coatings a high temperature cannot be achieved. At high temperatures, a selective coating is much better; and also high temperatures can only be achieved by selective coatings. Selective coatings with two glass covers have a better performance at high temperatures than selective coatings with one glass cover.

The performance of selective coatings with one glass cover is better than that of nonselective coatings with two glass covers. The curves for these cases are parallel with the former above the latter.

Therefore, the performance of nonselective coatings is equivalent to that of selective coatings for low temperature applications, but a selective coating is required for working in the high temperature range of applications.

SELECTIVE COATINGS ON COPPER SUBSTRATE

Coatings of black copper (41) and nickel black are used on copper substrates. But nowadays the black chrome coating developed by McDonald (15) is utilized by Driver et al. (16) as a selective coating on copper substrate. Harding (20) has utilized an interference filter of DC reactively sputtered metal carbide deposited on bulk copper substrate. This coating is stable at very high temperatures.

Black copper is obtained by chemical oxidation of copper with a solution containing sodium hydroxide and sodium chlorite. A surface of Cu_xO_y is obtained on copper substrate. A black coating of nickel black, which is a combination of sulphides of nickel and zinc, was first obtained by Tabor. Nickel is first electroplated on copper and then a coating of nickel black is electrodeposited from an electrolyte containing nickel sulphate, zinc sulphate, ammonium sulphate, ammonium thiocyanate and citric acid.

A selective coating of chrome black on copper substrate is also obtained by an electrodeposition technique from an electrolyte which is commercially available under the trade name CHROMONYX from M/S Harshaw Chemical Company (USA) or from an electrolyte consisting of chromium trioxide, sodium hydroxide, fluosilicic acid, sucrose and barium carbonate in appropriate compositions.

Fig. 4 illustrates the spectral reflectance of various coatings on copper substrate. Table 1 shows the absorptance (α) and emittance (ε) of various coatings on copper substrate.

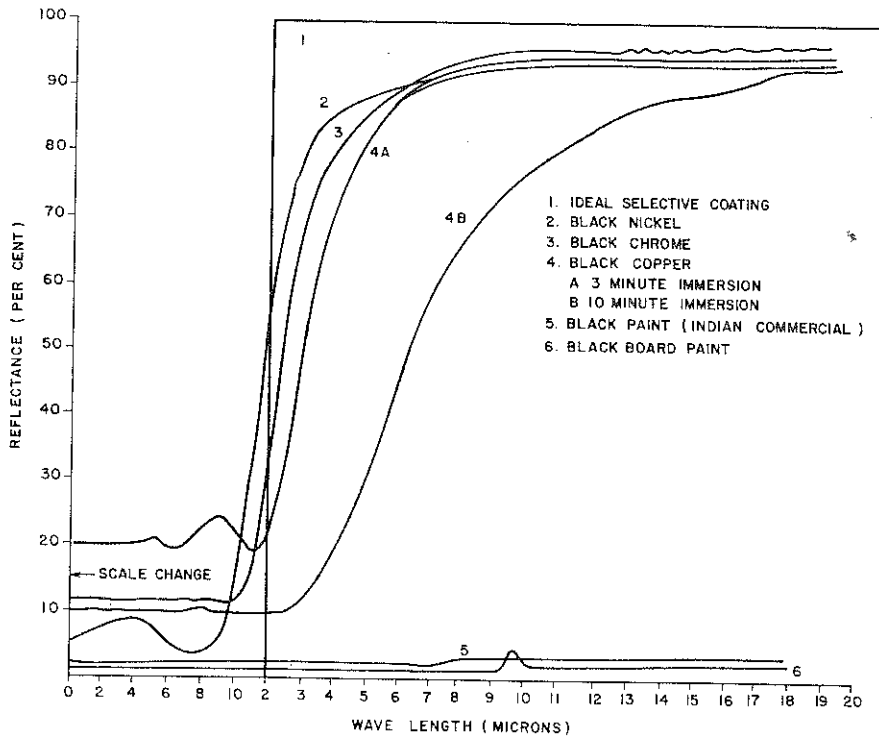


Fig. 4. Reflectance of coatings on copper substrate

Table 1. Absorptance and emittance of various coatings on copper substrate

Type of coating	Deposition technique	α	ϵ	Reference
Black copper	Chemical oxidation			
	(3 min. immersion)	0.79	0.05	4,12
	(10 min. immersion)	0.90	0.20	
Nickel black	Electrodeposition	0.85	0.05	1
Chrome black	Electrodeposition	0.823	0.044	16
Metal carbide	Interference filter	0.80	0.02	20
Black paint	Spraying & Painting	0.95	0.95	-

SELECTIVE COATINGS ON ALUMINIUM SUBSTRATE

There are so many coatings tested on aluminium substrate by electrodeposition, immersion, spraying and vacuum deposition techniques. Among these coatings black copper (13, 9, 7), black nickel (1) are used on aluminium. But nowadays chrome black (15) is replacing all coatings. Table 2 shows the absorptance and emittance of various coatings tested on aluminium foils, and Fig. 5 illustrates the spectral reflectance of various coatings on aluminium substrate.

Out of these coatings black copper and nickel black are used on aluminium. Recently McDonald (15) has utilised chrome black as a selective coating on aluminium substrate.

Table 2. Absorptance and emittance of various coatings on aluminium

Type of coating	Deposition technique	α	ϵ	Reference
SiO ₂ /Al/SiO ₂	Vacuum deposited	0.9	0.1	10
Cu _x O _y	Chemical conversion	0.85	0.11	9,7
Cu _x O _y	Spray	0.93	0.11	13
Cu _x O _y	Electrodeposited	0.85	0.11	9
Nickel black	Electrodeposited	0.877	0.066	9
PbS	Paint	0.89	0.20	6
Chrome black	Electrodeposited	0.868	0.088	15
Al ₂ O ₃ /MoO _x /Al ₂ O ₃	Vacuum deposited	0.91	0.085	11
Alcoa	Chemical conversion	0.93	0.35	18

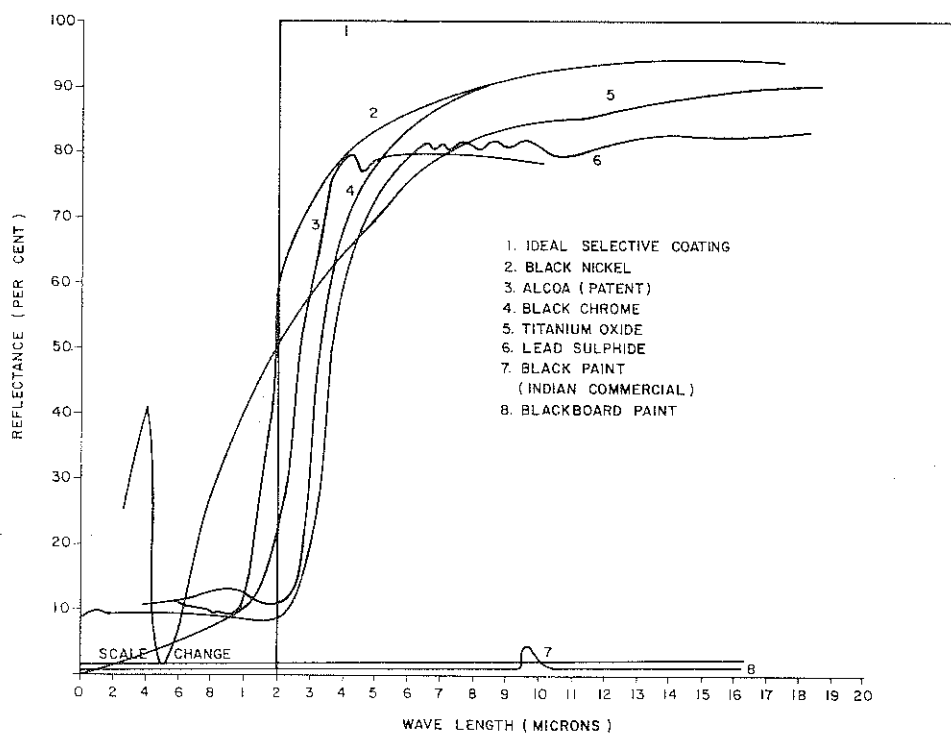


Fig. 5. Reflectance of coatings on aluminium substrate

Hottel and Unger (13) have developed selective coatings of black copper by spraying cupric nitrate on aluminium foils; on heating it to 350°C a coating of Cu_xO_y is obtained. Tabor (9) has utilised the immersion technique. Aluminium is first oxidised by anodising and then the sheet is immersed in solution containing cupric nitrate, potassium permanganate and nitric acid. Aluminium foils are dried and heated to 450°C, and coatings of Cu_xO_y on aluminium are obtained.

McDonald (15) has developed chrome black coatings on aluminium and steel panels. Aluminium foil is cleaned, zincated and then nickel is electroplated on it. After this treatment chrome black, which is commercially available (CHROMONYX) from M/S Harshaw Chemical Company, is electrodeposited. The foil is then rinsed with water and alcohol and dried in air.

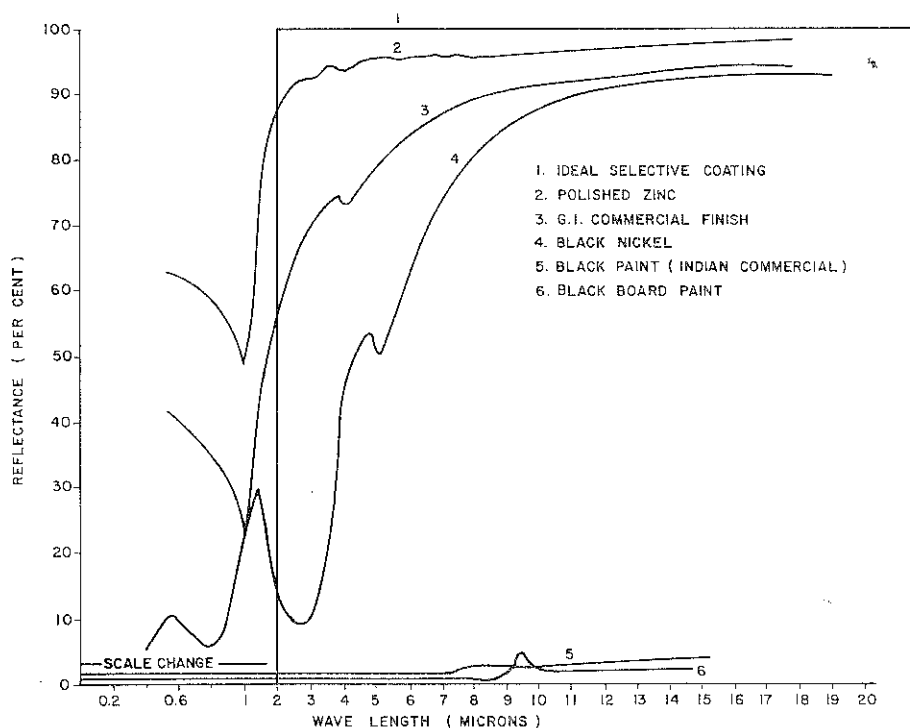


Fig. 6. Reflectance of coatings on galvanised iron substrate

SELECTIVE COATINGS ON GALVANISED IRON

Tabor (9) has developed black nickel as a selective coating on galvanised iron. Fig. 6 illustrates the spectral reflectance of various coatings on galvanised iron sheets. Table 3 shows the absorptance and emittance of various coatings on galvanised iron.

Table 3. Absorptance and emittance of various coatings on galvanised iron

Type of coating	Deposition technique	α	ϵ	Reference
Nickel black	Electrodeposited	0.89	0.12	9
Polished zinc	Electrodeposited	0.50	0.05	42
Chrome black	Electrodeposited	-	-	19

Gogna et al. (19) have developed recently a chrome black coating on galvanised iron. The coating of black chrome on metal sheet is directly electrodeposited. No treatment of zincating and nickel plating is necessary as required on aluminium substrate.

STABILITY AND DURABILITY OF VARIOUS COATINGS

It has been observed that black nickel and black copper coatings are deteriorated by moisture. A black copper coating is not stable at high temperature. But chrome black is a stable coating. Driver et al. (16) and McDonald (43) have reported that after heating for a long time this coating is stable at high temperatures. Of course, its selectivity is reduced slightly but still it is the best coating. Some of the properties of black chrome, black nickel and black copper and the microstructure of the layer have been recently studied by Bhide et al. (44).

COST OF COATINGS FOR SOLAR COLLECTORS

Winter and Fitzgerald (45) have theoretically calculated the cost incentive for selective absorbers. He has given a number of tables in his paper for the total collection of energy for a year for coatings of various thermal emittance and solar absorptance values. From these tables the cost incentive for coating can be calculated. McDonald (46) has reported the cost of various coatings which are shown in Table 4. From this table it is seen that the cost of black chrome is not very high as compared to nonselective coatings.

Table 4. Cost of coatings for solar collectors

Coating	Cost US\$/m ²	Absorptance	Emittance
Alkyd enamel	5.38	0.9	0.9
Ceramic enamel	5.38-6.45	0.9	0.5
Black chrome	7.53-8.61	0.9	0.1
Black copper (Black metal not included)	5.38	0.9	0.1
Black zinc	7.53-8.61	0.9	0.1
Black nickel	-	0.9	0.1
Maxorb	10.75	0.98	0.09

Williams (47) has reported the cost per unit area of collector for various glazings and coatings. Table 5 shows some of the values he has reported. From this table it is clear that the cost of collectors with selective coating increases by 12 percent, but energy gain increases

Table 5. Comparison of cost/performance parameters

Glass type	Coating type	Energy gain W	Cost \$/m ²	W/m ²	(W/m ²)/(\$/m ²)
Water white 3 mm	Black chrome	982	119.17	440.3	3.409
Furco 3 mm	Black chrome	969	119.59	434.4	3.632
Water white 3 mm	Black copper	906	119.48	405.0	3.390
Furco 3 mm	Black copper	890	109.90	399.0	3.630
Water white 3 mm	3M paint	430	116.25	192.6	1.657
Furco 3 mm	3M paint	415	106.67	186.2	1.746
Water white 3 mm	Cladwell paint	476	113.02	213.4	1.888
Furco 3 mm	Cladwell paint	462	103.44	207.0	2.001

by 133 percent. Tabor has also reported that the cost of the collector is increased by 5 percent if a selective coating is used but the increase in efficiency is 10 percent and high temperatures can be achieved; therefore, this increase in cost is compensated.

The calculations in Table 5 have been done for the following parameters:

Ambient temperature = 32.2°C, flow rate 2.18 litres/min,
inlet temperature = 98.8°C, and wind speed 11.2 km/hr.

Cover	Absorber	
Water white 3 mm $\tau = 0.913$	Black chrome	$\alpha = 0.93$
		$\epsilon = 0.08$
Furco 3 mm $\tau = 0.906$	Black cover	$\alpha = 0.90$
		$\epsilon = 0.12$
	Cladwell paint	$\alpha = 0.90$
		$\epsilon = 0.58$
	3M paint	$\alpha = 0.95$
		$\epsilon = 0.95$

CONCLUSIONS

The coatings used as selective black are very thin and these coatings do not provide any protection to the collector against atmospheric corrosion or thermal oxidation. Therefore, not only the coating but also the substrate should be chemically and thermally stable.

It is very difficult to find a selective surface suitable for use in collectors having no protective windows. But this limitation is not very serious because bare collectors are used only for low temperature applications such as swimming pool heating, etc.

Even in collectors that have glass windows, condensation on the collector plate should be avoided as very few low cost materials are unaffected by condensation even if they are not greatly affected by humidity.

Black nickel and black chrome were both known in the fifties, but black nickel was used instead of black chrome because formation of the latter requires current densities as high as 100 times those for the former. For a full size collector plate the rectifier needed becomes very large and so there is the problem of cooling the bath.

At high temperatures black copper and black nickel deteriorate but black chrome is thermally stable. Therefore, there is a need to develop a black chrome bath which can operate at a higher temperature and at low current densities.

Also if the cost of Maxorb foil (converted nickel foil) is reduced it will be a boon in the solar industry because of its superiority to other coatings.

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