

Selective electroplated chromium blacks

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The electrodeposition of chrome black selective surfaces on polished metal substrates has been studied by measuring the properties of samples as a function of plating time. Optical measurements show that in the first 50 sec a lossy dielectric film (apparently Cr_2O_3) of $0.6\text{-}\mu\text{m}$ thickness is deposited. The weights of deposits and their emittances, as well as the surface profiles of the samples, show that most ($0.4\text{--}0.5\text{ }\mu\text{m}$) of this dielectric film falls off between 50-sec and 60-sec plating time. An absorbing layer of chromium metal particles is then deposited on the remaining dielectric film to produce the high solar absorptance characteristic of these films. Calculations based on a particulate chromium deposit linearly graded with air using a recent theory of McKenzie and McPhedran are able to reproduce the film properties with deposit weights similar to those actually measured. It is shown that the thickness of the dielectric layer left under the particulate chromium deposit is important in obtaining the optimum performance in the trade-off between solar absorptance and thermal emittance.

Introduction

Many selective surfaces have been suggested or developed since the early work of Tabor,¹ particularly in recent years with the upsurge of research into solar energy utilization.¹⁻⁷ Selective surfaces can substantially improve the performance of ordinary flat plate collectors and yield dramatic improvements in extraction temperatures when used in evacuated collectors.

Probably the most popular selective surface being used today is based on the electroplating of black chrome.⁵⁻⁷ These coatings on electroplated nickel substrates have thermal emittances of the order of $0.06\text{--}0.15$, satisfactory for flat plate collectors, and solar absorptances of $0.96\text{--}0.98$. This high solar absorptance is the most distinctive feature of this coating and effectively sets a high standard for other selective surfaces to match. The origin of this high solar absorptance is not clear, and, indeed, little is known of the physical mechanisms operating in these films.

An experimental investigation of electroplated chrome black films has been carried out by Sowell and Mattox.⁷ They found that the films did not show optical interference effects. The composition profile was determined by means of the Auger technique combined

with sputter etching. The highest chromium-to-oxygen ratio was found at the interface between the coating and the nickel substrate, with the ratio approaching that for Cr_2O_3 at the surface-air interface. They decided that the coating had a continuously varying chromium-oxygen composition consisting of chromium particles in an amorphous or extremely fine grained oxide phase.

Other relevant work includes the investigation by Harding of chromium metal smokes,⁸ and by Fan and Spura⁹ of sputtered chromium-chromium oxide cermet. Harding found that particulate chromium films on copper substrates, prepared by evaporation of chromium in finite pressures of inert gas, were selective. Interference effects were observed in reflectance measurements. In general, the films had emittances greater than 0.15 if sufficiently thick to absorb more than 0.90 of the solar radiation. Fan and Spura suggested that electroplated chrome blacks could be modeled as a cermet interference layer (29% by volume Cr, the rest of Cr_2O_3) of $650\text{-}\text{\AA}$ thickness with a $350\text{-}\text{\AA}$ Cr_2O_3 AR layer on top. Such a model could not reproduce the high solar absorptance of >0.95 observed in chrome blacks.

The object of the study reported here was to determine in more detail the physical mechanisms responsible for the high solar absorptance of a particular series of electroplated chrome blacks. The technique used was to measure the optical properties (spectral reflectance, solar absorptance, and thermal emittance) and surface topography of films of varying thickness produced by plating for various lengths of time. Three stages in formation have been identified, each introducing an effect contributing to producing the black

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film. The behavior is much more complex than was observed by Sowell and Mattox or than can be explained by the work of Fan and Spura.

A model—capable of explaining the optical properties, based on a graded particulate chromium film on a dielectric film on the substrate—is described and justified experimentally and theoretically. The model uses recent theoretical improvements by McKenzie and McPhedran^{10,11} on the well known Maxwell-Garnett formula to describe the dielectric properties of the particulate film and allows one to predict how to obtain optimum properties for these commercially important surfaces.

Experimental Techniques

Sample Preparation

To do meaningful measurements on the reflectance of samples, it is important that they be prepared in a reproducible fashion on highly polished substrates. Copper blanks (100 mm × 50 mm) were mechanically polished using wet and dry carborundum paper, 6 μ m diamond paste and finally a proprietary mixture of Balzers #1. The highly polished samples were electroplated with nickel and with the chrome black according to the following steps:

- (a) Degreased by dipping in chloroform.
- (b) Electrocleaned as the cathode in an alkaline cleaner¹² at 60°C for 5 min. at 5 A with nickel anodes.
- (c) Rinsed.
- (d) Nickel plated using the Weisberg bath¹³ at 60°C for 5 min. at 5 A with nickel anodes.
- (e) Rinsed, distilled water rinsed, acetone rinsed, chloroform rinsed, and hot air dried. A drop of clear varnish was placed on the polished surface about 15 mm below the top edge. Hot air dried.
- (f) Weighed.
- (g) Dipped into chloroform, just avoiding immersion of the varnished area. Hot air dried.
- (h) Plated with black chrome at $23 \pm 2^\circ\text{C}$ for the time required at 10 A. Only the polished side was plated, with one lead anode being used. Bath composition¹⁴ was

CrO ₃	400 g/liter,
NaOH	60 g/liter,
H ₂ SiF ₆	0.5 g/liter,
Sucrose	2.5 g/liter, and
BaCO ₃	7.5 g/liter.
- (i) Rinsed, distilled water rinsed, acetone rinsed, and hot air dried.
- (j) Weighed.

It was found in the course of this work that the electroplated nickel film assisted in obtaining satisfactory films. Attempts to electroplate chrome black onto samples which were nickel coated by vacuum evaporation resulted in poor films even after long plating times.

Experimental Apparatus

Thermal emittances were measured using two techniques. One, a rotating heated cavity emissometer,¹⁵

gave a measure of the emittance at 30°C. The other, a Land surface thermometer, was used to measure the emittance at 80°C, the sample being heated to that temperature on a hot plate. Both instruments were calibrated using samples of known emittance. The solar absorptance was obtained from a measure of the integrated solar reflectance. A quartz iodide lamp (GE ELH) simulating AM2 solar radiation¹⁶ was used in conjunction with an integrating sphere to illuminate the sample diffusely while viewing the radiation reflected normally.

The visible and near ir reflectances as a function of wavelength from 0.4 μ m to 2.5 μ m were measured using a Beckman DK2 spectrophotometer with an integrating sphere. The radiation was incident normally on the sample, and the integrated reflected radiation was measured. The far ir specular reflectances at 30° angle of incidence over the 1–16- μ m wavelength range were obtained using a Beckman IR4 spectrophotometer.

Results

It was seen by visual inspection that the samples plated for 20–50 sec were specular with interference colors typical of dielectric films, those plated for 50–60 sec looked nonspecular and gray, and those plated for longer than 60 sec were specular and black. Some samples showed all three regions due to the higher plating current toward the edges of the samples. The dielectric film was in the center, the black film was around the outside, and the gray area was in between.

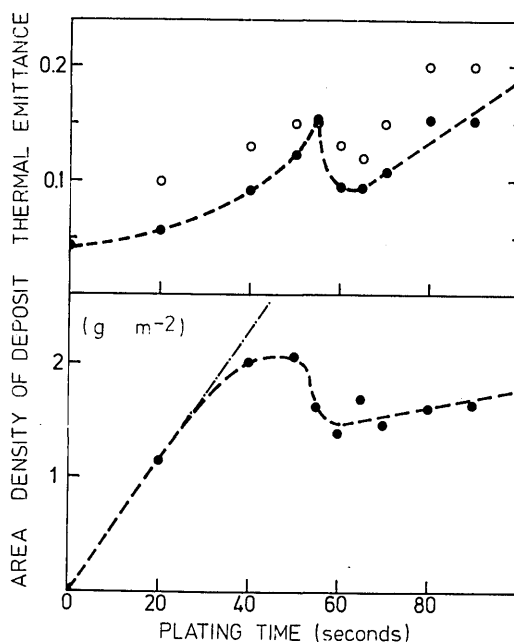


Fig. 1. The thermal emittance at 30°C (closed circles), measured using a rotating cavity emissometer,¹⁵ and the thermal emittance at 80°C (open circles), measured using a Land surface thermometer, are given for the central region of the sample as a function of plating time. The area density computed from the total deposit mass is shown also as a function of plating time.

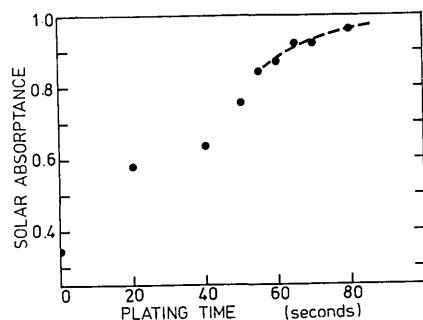


Fig. 2. The solar absorbance is shown as a function of plating time for the films.

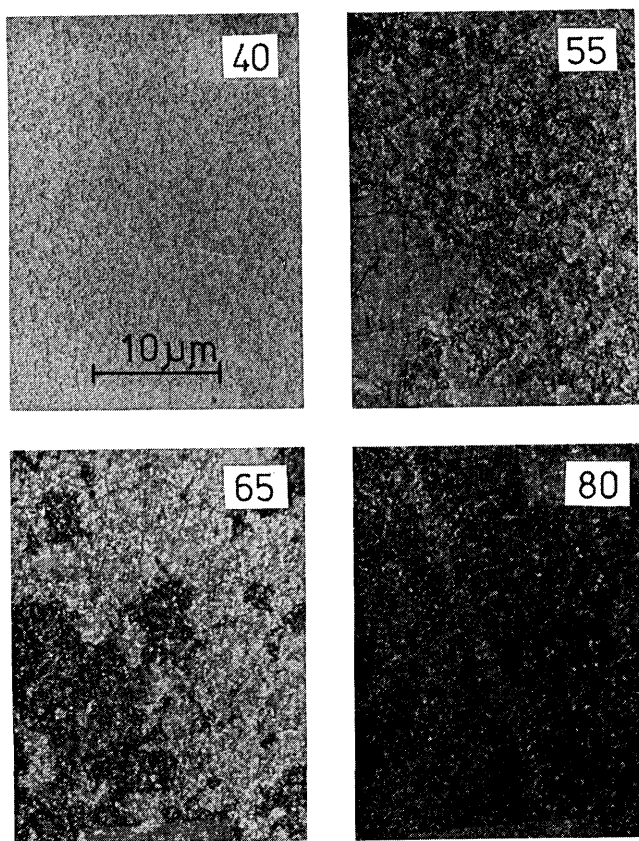


Fig. 3. Optical micrographs of four samples are shown. The samples are labeled by the times of plating. Sample 40 shows the uniform dielectric film with some pitting, sample 55 shows large regions where the dielectric film has fallen off, sample 65 shows regions where the black particulate chromium film is on the reduced dielectric layer, and sample 80 shows the surface completely covered by the particulate material.

In Fig. 1 the weights of film deposited on the samples and the thermal emittances of the samples at 30°C and 80°C are shown as a function of plating time. The most interesting feature of the weights and of the emittances is the marked change in behavior near the plating time of 55 sec—this corresponds to the dielectric-to-gray transition.

The weights plotted in Fig. 1 are the weights of the coating over the whole sample and, because of the inhomogeneities in plating density across the films, are not completely typical of the central region of the sample. The over-all features do, however, reflect the behavior in the central region. The actual weight on the sample plated for 55 sec is half of that which would be expected from extrapolating the initial rate of weight increased to this time.

The abrupt change in emittance at a plating time of 55 sec (Fig. 1) corresponds to the drop in deposited weight, and, because only the central region of the sample is measured in the emissometer, the change is much sharper. Indeed, if the increase in emittance over that of the substrate is linearly dependent on the weight of the deposited film, the decrease in emittance at 55 sec corresponds to a thickness decrease of ~60%. The higher emittances using the Land thermometer were due to the higher sample temperature.

In Fig. 2, the integrated solar absorbance is shown

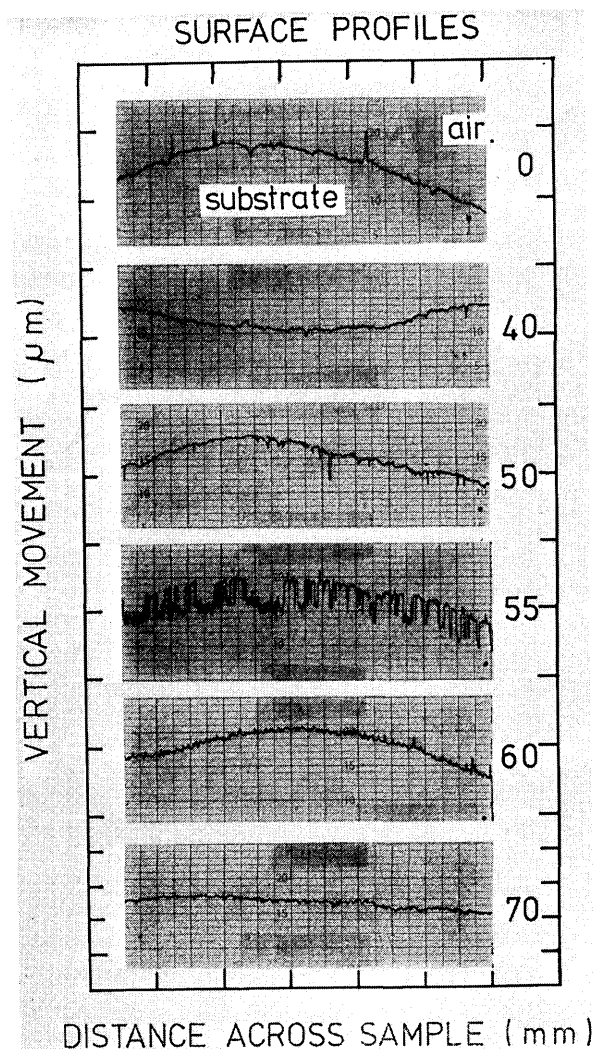


Fig. 4. Surface profile scans obtained using a Talysurf instrument are shown of samples coated for various times.

Table I. Center Line Average Roughness

Plating time (sec)	0	20	40	50	55	80
CLA (nm)	44	35	34	32	120	47

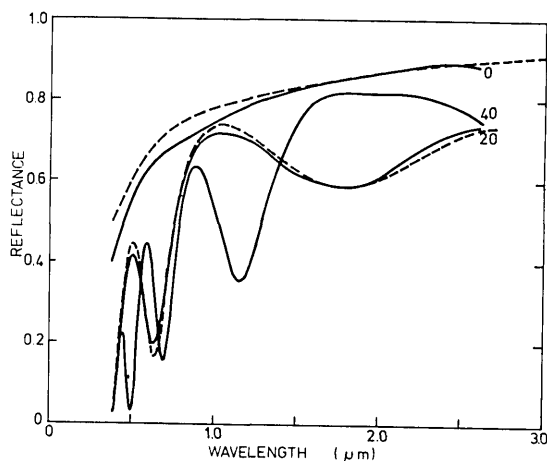


Fig. 5. Integrated reflectance curves are shown as a function of wavelength for samples plated for 0 sec, 20 sec, and 40 sec. The dashed curves are explained in the text.

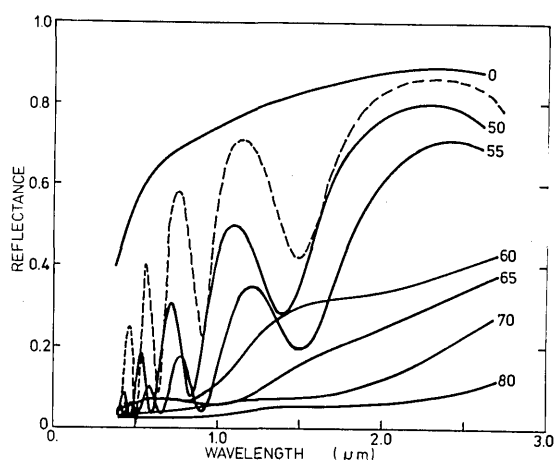


Fig. 6. Integrated reflectance curves are shown as a function of wavelength for samples plated for 0, 50, 55, 60, 65, 70, and 80 sec. The dashed curve is that calculated for a uniform dielectric film of 0.60- μ m thickness with dielectric constant as in Fig. 8.

as a function of plating time. The optimum thickness of the film occurs soon after the sudden decrease in emittance. The emittance is then at its minimum while the solar absorptance is greater than 0.90. As the plating continues, both the solar absorptance and the thermal emittance of the film increase.

The different regions of the sample were viewed under an optical microscope. Figure 3 shows black and white reproductions of color photographs of each of the three regions and the intermediate regions. The color photographs showed, in the case of region 1, a uniform color (green) with some pitting of a different color (red); in the case of region 2, a mosaic of different colors; and,

in the case of region 3, black particles densely covering the mosaic pattern.

Information concerning the surface topography was obtained using a Talysurf instrument. The surface profiling stylus used in the measurements had a tip radius of 2.5 μ m, and hence only features coarser than this would be observed. In Fig. 4, the surface profiles obtained across the centers of the samples are shown. Notice the large vertical magnification normal to the film and the small magnification in the plane of the film. From the Talysurf scans, the center line average roughness (arithmetic mean of deviations from center line) was obtained and is shown in Table I.

Note the dramatic increase in roughness for the sample after plating for 55 sec. The profile of this sample in Fig. 4 yields peak-to-peak changes in thickness of 0.4–0.5 μ m across the sample. The results are consistent with a major part of the dielectric film falling off at a time of 50–55 sec.

The thicknesses of the dielectric films were measured using optical interference. Before electroplating, a small spot (\sim 3-mm o.d.) of varnish was placed on the nickel film; after electroplating this was dissolved in solvent, leaving a step from plated to unplated area. The thicknesses were determined, using a Watson interferometer, as 0.25 ± 0.03 μ m for sample 20 and 0.50 ± 0.03 μ m for sample 40.

In Figs. 5 and 6 are shown the integrated reflectance spectra of the samples obtained using the Beckman DK2 instrument. The reflectance of a diffuse MgO reflector was taken as the 100% line. For samples 20, 40, 50, and 55, oscillations in reflectance with wavelength, characteristic of interference layers, are observed. The samples plated for longer times do not show such sharp features.

The ir specular reflectances from 1 μ m to 10 μ m are shown in Fig. 7 for some of the samples. For this reflectance measurement, the sample beam undergoes two reflections on aluminum mirrors as well as the reflection from the sample. The reflectance curve for an aluminum mirror placed in the sample position is given, and the data can be converted to absolute reflectances using tabulated data for aluminum.

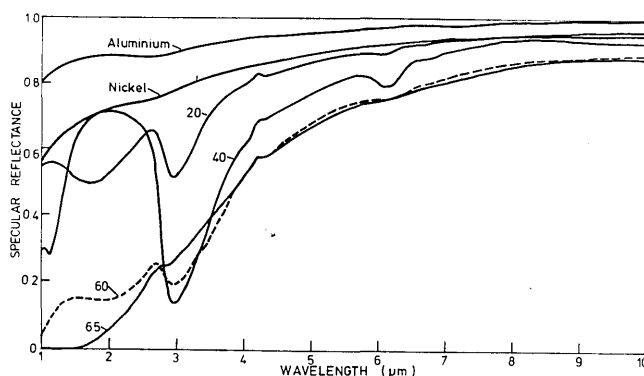


Fig. 7. The specular reflectance of some of the samples at 1–10- μ m wavelength is given. The samples are labeled by their plating times.

The curve for a clean aluminum mirror is given as a calibration.

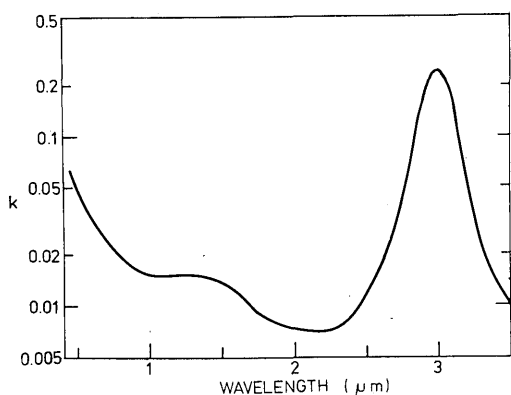


Fig. 8. The imaginary part (k) of the refractive index used to derive the fitted curves in Figs. 5 and 6 is shown as a function of wavelength. The real part of the refractive index (n) was held constant at 1.8.

Discussion

Dielectric Films

The reflectance of the electroplated nickel substrate (Fig. 5) is in reasonable agreement with the values reported by Johnson and Christy¹⁷ (dashed curve), and the values of n and k derived by these authors have been used to characterize the substrate in subsequent calculations.

The films obtained at short deposition times are basically uniform films and can be characterized by a thickness and by a wavelength dependent refractive index ($n - ik$). For a film where k is small, the reflectance minima occur at wavelengths λ given in a first approximation by $nd = (2m + 1)\lambda/4$, where m is an integer, and d is the thickness. It is difficult to regress from the reflectance data to derive the values of n and k as, at each wavelength, at least two independent data must be known. We have assumed samples 20 and 40 to be composed of the same material but to be of different thicknesses and have used the reflectances in Figs. 5 and 7 as these data. It is also assumed that n is wavelength independent and that the behavior of k is determined by several Lorentzian oscillators. If $n = 1.8$, there is least spread in the values of k obtained for the two films, and, for this value of n , three Lorentzian lines at different wavelengths are needed to fit k . The curve for k as a function of wavelength is shown in Fig. 8, and a fitted reflectance curve using this and $n = 1.8$ is shown in Fig. 5 (dashed line). For n to equal 1.8 and the reflectance maxima and minima to be situated correctly, the thicknesses of the films should be $0.25 \mu\text{m}$ for sample 20 and $0.47 \mu\text{m}$ for sample 40, but this is in good agreement with the values measured above.

The composition of the dielectric layer is not known, but it is expected to be a nonstoichiometric oxide of chromium, possibly in a cermet form. Combining the thicknesses obtained above and the deposited area densities shown in Fig. 1 yields an upper limit of 4100 kg m^{-3} for the density at the center of the film; this is

compared with the 5100 kg m^{-3} characteristic of bulk Cr_2O_3 . The real part of the refractive index $n = 1.8$ is close to the 2–2.4 reported by Fan and Spura⁹ for sputtered Cr_2O_3 , and the wavelength dependence of the imaginary part k is similar to that of the absorption coefficient reported by these authors. Differences in density and refractive index of this magnitude in films prepared by different methods are commonly observed, and it is highly likely that the material is a fine grained Cr_2O_3 deposit, which would lower the effective refractive index of the film.

In the curve showing the wavelength dependence of k (Fig. 8) there is a strong resonance at $3 \mu\text{m}$. This resonance is observable in the data obtained by other authors for chrome blacks⁷ and is associated with the dielectric material in the film. The reflectance data for samples 20, 40, and 50 show the effect of this resonance; it is most evident in those samples where the first interference minimum in the reflectance occurs near $3 \mu\text{m}$.

Samples 50 and 55 show some interference colors when viewed, and maxima and minima occur in the visible and near ir reflectance spectra (Fig. 6). The samples are made up of regions of uniform dielectric and of regions where much of the dielectric film has fallen off. The reflectance of the sample will be made up of the sum of the reflectances of each region weighted with its area fraction. The spectrum of the uniform region can be calculated assuming n and k to be unchanged from the values for samples 20 and 40 and using the position of the reflectance minima to obtain the thickness. Such a calculated spectrum for a dielectric film $0.60 \mu\text{m}$ thick is shown in Fig. 6. It should be possible to obtain the spectrum of the area where the dielectric has fallen off by weighting the calculated spectrum and subtracting it from the data. Unfortunately, because of pitting of even the uniform film area, this calculation did not yield any useful results. The thicknesses of the major parts of the uniform dielectric films obtained from the position of the interference minima were $0.56 \mu\text{m}$ and $0.60 \mu\text{m}$ for samples 50 and 55, respectively.

The surface topography scan of sample 55 (Fig. 4) shows that the film thickness decreases from $0.60 \mu\text{m}$ by $0.4\text{--}0.5 \mu\text{m}$, leaving an irregular film of thickness $0.1\text{--}0.2 \mu\text{m}$. It is possible that even more of this dielectric film falls off with further plating, so $0.2 \mu\text{m}$ is to be regarded as an upper limit to its thickness. The color optical micrographs show a mosaic of colors, as would be expected if there were a thickness range of the dielectric film. Owing to this thickness fluctuation, there should be a large variation in current density across the surface, and, at this stage, probably because of the higher plating current densities, chromium particles are precipitated. Electron diffraction results of other workers show that metallic chromium makes up a large part of the final film.^{7,9}

Particulate Films

An essential part of the chrome black is the particulate nature of the chromium deposit on top of the film.

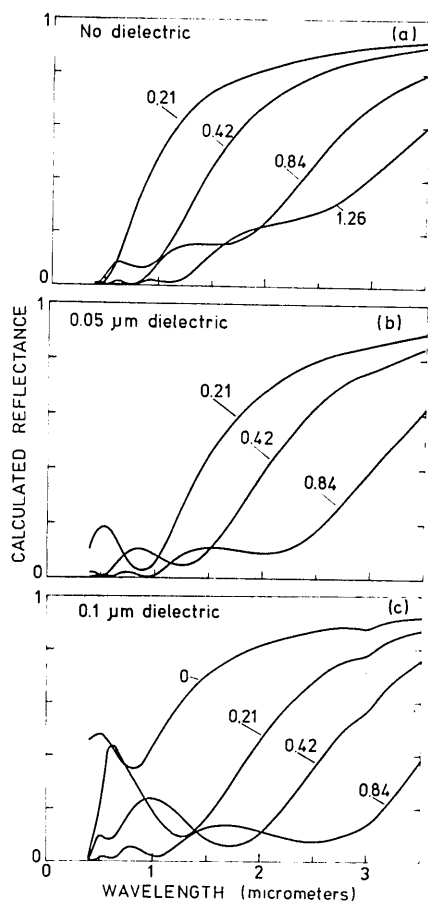


Fig. 9. Calculated reflectance curves are shown for linearly graded films of particulate chromium of varying area density on (a) no dielectric on nickel, (b) 0.05- μm dielectric on nickel, and (c) 0.1- μm dielectric on nickel. (A thickness of 0.1 μm of particulate chromium corresponds to an area density of 0.21 g m^{-2} .)

In our model we ignore any scattering by the chromium particles and treat the layer as an interference layer of chromium particles dispersed in air. There is also undoubtedly Cr_2O_3 present in the deposit, but, for simplicity, an air dielectric has been used.

The dielectric properties of dilute dispersions of small spherical particles of material i embedded in a matrix of material j is given by the Maxwell-Garnett formula

$$\frac{\epsilon - \epsilon_j}{\epsilon + 2\epsilon_j} = q \frac{\epsilon_i - \epsilon_j}{\epsilon_i + 2\epsilon_j},$$

where ϵ is the dielectric constant of the combination, and q is the volume fraction of i in j . This theory is limited in its area of application, being valid only when the spheres are well separated, i.e., only for small q (< 0.2). The application of this theory to situations where the spheres almost touch gives erroneous results. A more useful theory, valid for regular arrays of uniform spheres on cubic lattices, has been given by McKenzie and McPhedran.^{10,11} They extended an early theory due to Lord Rayleigh¹⁸ to include higher order correc-

tions to the Maxwell-Garnett formula produced by proximity effects. Although our samples are not made up of uniform spheres of chromium on a regular array, this model will be more correct than the Maxwell-Garnett formula, because some of the large effects of proximity are included. It is necessary to use this extended formula to obtain enough absorption in the chromium particle layer; the Maxwell-Garnett formula generally gives too low a value of k .¹⁰

Since the particles are almost touching in the most dense regions of the chromium film, we have used the formula for a simple cubic array of spherical particles with a maximum value of q corresponding to the particles touching one another. Because the exact derivation of the dielectric constant for large q involves a lengthy summation over many terms, the expansion has been terminated after the fourth term. This termination has the effect, in the ideal case of perfectly conducting spheres in vacuum, of shifting the divergence of the dielectric constant from $q = 0.52$ to $q = 0.59$,¹⁰ and, hence, to achieve a similar range of dielectric constant as a function of q , we have allowed the maximum value of q for the particulate metal film to be 0.59.

The existence of a particulate chromium film is, by itself, not sufficient to produce the high solar absorptances characteristic of chromium blacks. To achieve a high absorptance over a range of wavelengths a small change in refractive index at the air-film interface is necessary, otherwise a significant reflection loss will occur. This small change can be achieved for a uniform film by having a low volume fraction q of metal, and films made by the metal smoke method are possibly of this type.^{8,19,20} For more dense films a substantial improvement in the absorptance can be achieved by grading the composition q down to zero at the air-film interface.²¹ The electroplated chrome blacks are of this type. For simplicity, we have assumed the film to be particulate chromium mixed with air, with the volume fraction of chromium varying from 0.59 at the bottom to zero at the top of the layer. The dielectric constant ϵ was derived from q and the dielectric constant of chromium metal.¹⁷

Figure 9(a) shows the calculated spectra for linearly graded particulate chromium films on nickel substrates. The parameters shown on each curve are the mass per unit area of chromium deposit. The calculations were done by breaking up the layer into fifty uniform layers and solving numerically for each wavelength.²¹

These curves [Fig. 9(a)] are similar to those obtained by Harding⁸ for deposited chromium smokes of small particle size ($< 0.02 \mu\text{m}$), except that the area densities of the theoretical films need to be about 3 \times the measured area densities to achieve similar results. This discrepancy could be due to the effects of scattering on the experimental data and to the composition profile deviating from a linear grading. Figure 10 shows the calculated solar absorptances (assuming 5900-K blackbody radiation from the sun) as a function of the mass thickness of linearly graded chrome black on top.

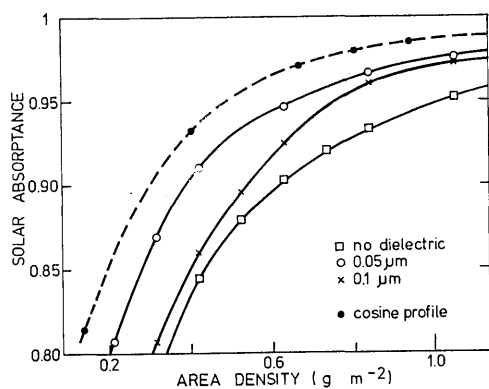


Fig. 10. Calculated solar absorptances of particulate chromium films on dielectric material on nickel substrates for normally incident radiation are shown as a function of the mass of particulate film deposited. The full curves are for particulate film linearly graded with air on 0- μm , 0.5- μm , or 0.1- μm dielectric on the nickel substrate (Fig. 9), and the dashed curve is for a particulate film graded with air in a cosine profile on 0.05- μm dielectric on the nickel substrate.

The calculated reflectance curves resemble the measured curves for the thickest electroplated films (Fig. 6), but the agreement is not good. The experimental data show an approximately uniform reflectance from 0.5 μm to 2.0 μm , while the calculations give a steadily increasing reflectance over this range. We have not yet included the effect of the dielectric underlayer on the behavior of the film. It is not obvious whether it will improve the performance of the film.

Composite Film Model

The presence of a dielectric layer under the chrome black will modify the absorbing properties of the film. This dielectric, according to experimental evidence, has a maximum thickness of 0.15–0.2 μm but could be considerably less thick.

In Figs. 9(b) and 9(c) are shown the calculated curves for reflectance as a function of wavelength for 0.1- μm and 0.05- μm thickness, respectively, of dielectric covered by linearly graded chrome black films; the corresponding calculated solar absorptances are shown in Fig. 10. The parameters labeling the curves are the area density of chrome black on top of the dielectric layer. Notice in Fig. 10 that the 0.05 μm of dielectric under the chrome black markedly increases the solar absorptance over that for no dielectric or 0.1- μm dielectric. The curves for 0.05 μm of dielectric [Fig. 9(b)] are consistent with those observed for electroplated chrome blacks in the last stages (samples 70, 80, and 90). This weight of dielectric (0.25 g m^{-2}) and the weight of chrome black for the heaviest coating (0.84 g m^{-2}) give 1.1- g m^{-2} total area density, in reasonable agreement with the observed weight after 90 sec of 1.7 g m^{-2} (Fig. 1).

This model contains the essential features of the chrome black surface, namely, a graded particulate chromium deposit on a 0.05- μm Cr_2O_3 layer. There are a number of additional factors that could be invoked to

improve the solar absorptance still further. The most important improvement is gained by altering the grading profile of the particulate chromium film. A linear grading from $q = 0.59$ at the bottom to $q = 0$ at the top has been assumed in the previous calculations, but other profiles are possible. A more dense film with q large over much of the layer, falling rapidly to zero at the air interface, seems likely.

We have calculated the solar absorptances of films with a cosine profile on top of 0- μm , 0.05- μm , and 0.1- μm dielectric films. For a position x measured from the dielectric film, the volume fraction q is $0.59 \cos[(\pi x)/(2T)]$, where T is the total linear thickness. This gives a more abrupt change in density at the air interface. The same trends as were observed for linearly graded films (Fig. 10) were obtained, i.e., solar absorptances greatest for dielectric films of 0.05- μm thickness. The calculations for this situation, with different thicknesses of chrome black, are shown in Fig. 10; the solar absorptance has been markedly improved by using a cosine rather than a linear profile. This improvement stems from convoluting the dependence of the dielectric constant on q , the volume fraction, with the dependence of q on depth in the film. Because ϵ changes rapidly with q for high q , the result of this convolution with the dependence of q on thickness leads to an approximately linear increase in the absorbing part of the dielectric constant, which is close to the optimum refractive index profile.²¹

Another effect which has been considered is the mixing, on a scale much smaller than wavelengths, of the particulate chromium deposit into the dielectric underlayer. After the dielectric layer falls off, the remaining dielectric could be rough on the submicron scale, and deposition of chromium particles in the low areas would lead to a gradation of the underlayer from dielectric to particulate chromium. Calculations including this effect by linearly grading the composition through the dielectric film increased the solar absorptance only slightly, so, although this may occur, it is not an essential part of the model.

As mentioned earlier, this model does not include any irregularities of dimensions 0.1 μm and above in the plane of the film. Variations in thickness of the dielectric and particulate films do occur, and the final spectrum should be the sum of a number of weighted spectra corresponding to these different thicknesses. Because the spectra are broad anyway, this additional broadening will not make much difference. The surface roughness of the dielectric film will act to increase the solar absorptance by reflecting normally incident radiation obliquely, forcing it to travel through more particulate chromium before leaving the film.

Optimization of Emittance and Absorptance

The optimization of the solar absorptance should be considered in conjunction with the optimization of the thermal emittance. Usually there is a trade-off between the two.

The 0.05- μm layer of dielectric which acts to increase the solar absorptance for the same mass of particulate

chromium also acts to decrease the thermal emittance. First, the thickness of the particulate film affects the thermal emittance because it is not completely transparent to thermal radiation. So the reduction in the chromium deposit required decreases the emittance. Second, for the same solar absorptance, the film with the $0.05\text{ }\mu\text{m}$ of dielectric on the bottom has the cut on wavelength from absorbing to reflecting behavior at shorter wavelengths, giving less overlap with the thermal spectrum. The cut on with wavelength is also sharper for this film (Fig. 9).

The optimum thickness for the dielectric film is, according to our calculations, close to $0.05\text{ }\mu\text{m}$, but a considerable range in this thickness from $0\text{ }\mu\text{m}$ to $0.1\text{ }\mu\text{m}$ could be tolerated with some degradation in performance. The control of the dielectric layer thickness would appear to be difficult as little is known about the various stages in the formation of the film. The peeling may be a result of stresses incorporated in the electroplating assisted by thermal stresses due to resistive heating of the deposit; but why the film builds up to $0.6\text{ }\mu\text{m}$ before peeling and then peels off only partly is not clear. The deposition of the chrome black is also related to the occurrence of the rough dielectric film after peeling.

The nature of the deposition process and our experiments confirm that surface finish governs the formation of the film. We could not obtain satisfactory films on highly polished substrates vacuum coated with nickel, yet satisfactory films can be produced on electroplated nickel; it seems that both the dielectric layer and the particulate layer prefer to deposit onto slightly roughened surfaces.

Conclusions

The following have been shown in the course of this work:

(a) Initially a layer of lossy dielectric material ($<0.6\text{ }\mu\text{m}$) similar to Cr_2O_3 is deposited in the electrodeposition of chrome blacks.

(b) This material is absorbing in the visible and shows some strong ir absorptances in the vicinity of $3\text{--}5\text{-}\mu\text{m}$ wavelength.

(c) The dielectric film builds up to $0.5\text{--}0.6\text{ }\mu\text{m}$ thick after $50\text{--}60\text{-sec}$ plating time, and then most of the film falls off. Only $0.05\text{--}0.15\text{ }\mu\text{m}$ of dielectric film is left after this process.

(d) A particulate chromium deposit is formed on the remaining dielectric film, and recent theoretical results^{10,11} have been used to explain the properties of this film.

(e) The absorptance due to the particulate chromium film dominates but the dielectric underlayer assists to obtain the maximum solar absorptance with the minimum thermal emittance. A thickness of $0.05\text{ }\mu\text{m}$

for the dielectric is shown by calculation to be close to the optimum. High solar absorptances are obtained for the thicknesses of the particulate chromium film near 1 gm^{-2} .

This work gives a reasonable accounting of the properties of these films based on what is known theoretically and experimentally. The essential features of the model are the graded layer of particulate chromium ($\sim 0.2\text{ }\mu\text{m}$) on top of a layer ($\sim 0.05\text{ }\mu\text{m}$) of dielectric material.

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