

Solar Spectral Optical Properties of Pigments

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November 1, 2004

Abstract

Owners of homes with pitched roofs visible from ground level often prefer non-white roofing products for aesthetic considerations. This paper reports on a collaborative research between LBNL and the industry for developing cool colored materials for sloped roofs. The suitability of a pigment for inclusion in “cool” colored coatings with high solar reflectance can be determined from its solar spectral backscattering and absorption coefficients. Pigment characterization is performed by dispersing the pigment into a transparent film, and then measuring spectral transmittance and reflectance. Measurements of the reflectance of film samples on black and white substrates are also used. Various pigments are characterized by determination of absorption and backscattering coefficients as functions of wavelength in the solar spectral range of 300 to 2500 nm. Pigments in widespread use are examined, with particular emphasis on those that may be useful for formulating non-white materials that can reflect the near-infrared (NIR) portion of sunlight, such as the complex inorganic color pigments (mixed metal oxides). These materials remain cooler in sunlight than comparable colors. NIR-absorptive pigments are to be avoided. High NIR reflectance can be produced by a reflective metal substrate, a NIR-reflective underlayer, or directly by the use of a pigment that scatters strongly in the NIR.

1 Introduction

Nonwhite pigments with high near-infrared (NIR) reflectance historically have been used to camouflage military surfaces (by mimicking foliage) and to minimize solar heating of dark exterior architectural surfaces, such as colored vinyl siding and gray battleship hulls [1, 2, 3]. In recent years roofing manufacturers have incorporated NIR-reflecting pigments in coatings applied to a variety of nonwhite roofing products, such as metal panels and clay tiles [4, 5, 6, 7, 8, 9]. In this

paper we compute the solar spectral absorption and backscattering coefficients of a wide variety of pigments that may be used in architectural coatings.

Visible light (400 - 700 nm) accounts for only 43% of the energy in the air-mass 1.5 global solar irradiance spectrum (300 - 2500 nm) typical of North-American insolation [10]; the remainder arrives as near-infrared (700 - 2500 nm, 52%) or ultraviolet (300 - 400 nm, 5%) radiation (Fig. 1). Hence, replacing NIR-absorbing (“conventional”) roofing with visually similar, infrared-reflecting (“cool”) roofing can significantly reduce building heat gain.

A cool coating must have low visible transmittance to hide its background and low NIR absorptance to minimize NIR heat gain. Cool films may be subclassified as either “NIR-reflecting” or “NIR-transmitting.” An NIR-reflecting film is always cool, while an NIR-transmitting film requires an NIR-reflecting background (e.g., a shiny metal or a white coating) to form a colored NIR-reflecting composite [1, 11].

A paint is a dispersion of pigment particles (e.g., titania) in a clear binder, such as acrylic. The propagation of light through pigmented coatings is of natural interest to the coating and colorant industries, and has been extensively studied over the past century. One of the simplest and most popular continuum models is the two-flux theory introduced by Schuster in 1905 [12] and popularized by Kubelka and Munk [13, 14, 15, 16, 17]. The Kubelka-Munk (K-M) model describes the one-dimensional, bidirectional propagation of diffuse light through a film by parameterizing the rates at which the film absorbs and/or backscatters light.

We compute absorption and backscattering coefficients from spectrometer measurements of film reflectance and transmittance. We examine 87 pigmented coatings, identifying both cool pigments—i.e., those that can be used to make NIR-reflecting or NIR-transmitting cool coatings—and pigments that should be excluded from cool coatings. Our goal is to provide complete solar spectral absorption and backscattering coefficients describing a large palette of pigments usable for architectural coatings.

2 Theory

The purpose of our measurements and model of radiant transfer in single-pigment coatings is to obtain backscattering and absorption coefficients S and K that approximately characterize the

pigment. High precision is not the goal, but a reliable general characterization of each individual pigment is. We cover the solar spectral region from 300 to 2500 nm at 5-nm intervals. Each wavelength is treated independently of all others except for the use of the forward scattering ratio. Since the K-M model applies to diffuse illumination, whereas we are using collimated radiation, the treatment may be expected to be more accurate in strongly scattering films in which a fully diffuse radiation field quickly develops. However, we have used a formulation in which a non-scattering pigment (e.g., a dye) is assigned a K value approximating Beer's law for diffuse radiation traversing a slab. In summary, we are not expecting precise characterization, but expect to extract consistent, reliable, and practical information for each pigment.

The one-dimensional propagation of light through a coating is approximated by the two-flux *Kubelka-Munk* (K-M) theory, in which downward and upward beams can be absorbed and/or backscattered as they traverse the film. All light in the film is assumed to be diffuse (subscript d), either because the film is diffusely illuminated, or because the film is strongly scattering. The downward diffuse flux $i_d(z)$ and upward diffuse flux $j_d(z)$ within the film are modelled by

$$-\frac{di_d}{dz} = -(K + S)i_d + Sj_d \quad (1)$$

$$\frac{dj_d}{dz} = -(K + S)j_d + Si_d \quad (2)$$

where K and S are coefficients of absorption and backscattering, respectively. The fluxes and coefficients are wavelength-specific.

Our theory and algorithm for computing the coefficients K and S from measurements of the reflectance and transmittance of pigmented coatings in contact with air (i.e., paint films in a spectrometer) are detailed in [18].

3 Experiment

The optical properties of 87 pigment films—4 white, 21 black or brown, 14 blue or purple, 11 green, 9 red or orange, 14 yellow, and 14 pearlescent—were characterized by computing spectral K-M coefficients and non-spectral forward scattering ratios from spectral measurements of film reflectance and transmittance. Our methodology is detailed in [18].

4 Pigment Classification

For convenience in presentation, the pigments were grouped by color “family” (e.g., green) and then categorized by chemistry (e.g., chromium oxide green). Some families span two colors (e.g., black/brown) because it is difficult to consistently identify color based on pigment name and color index (convention for identifying colorants [19]). For example, a dark pigment may be marketed as “black,” but carry a “pigment brown” color index designation and exhibit red tones more characteristic of brown than of black. Pigment categories are presented in the order of simpler inorganics, more complex inorganics, and then finally organics. Each member of a color family is assigned an identification code Xnn , where X is the color family abbreviation and nn is a serial number. For example, the 11 members of the green color family (“G”) have identification codes G01 through G11. The same pigment may be present in more than one pigmented film. For example, our survey includes four titanium dioxide white films (W01-W04). However, the concentration of pigment, pigment particle size, and/or source of the pigment (manufacturer) may vary from film to film.

5 Pigment Properties by Color and Category

Table 1 summarizes some relevant bulk properties of the pigmented films in each category, such as NIR reflectances over black and white backgrounds. The measured and computed spectral properties of each pigmented film (reflectance, transmittance, absorptance, absorption coefficient, and scattering coefficient) are charted in [20].

When examining spectral optical properties, it is worth noting that most of the NIR radiation in sunlight arrives at the shorter NIR wavelengths. Of the 52% of solar energy delivered in the NIR spectrum (700 - 2500 nm), 50% lies within 700 - 1000 nm; 30% lies within 1000 - 1500 nm; and 20% lies within 1500 - 2500 nm (Fig. 1). We refer to the 700 - 1000 nm region containing half the NIR solar energy (and a quarter of the total solar energy) as the “short” NIR.

In the discussions below, black and white *backgrounds* are assumed to be opaque, with observed NIR reflectances of 0.04 and 0.87, respectively. Note that in the absence of the air-film interface, the continuous refractive index (CRI) NIR reflectances of the black and white backgrounds are 0.00 and 0.94, respectively.

5.1 White

All four whites were titanium dioxide (TiO_2) rutile. Other white pigments (not characterized in this study) include zinc oxide, zinc sulfide, antimony oxide, zirconium oxide, zirconium silicate (zircon), and the anatase phase of TiO_2 .

TiO_2 rutile is a strongly scattering, weakly absorbing, stable, inert, nontoxic, inexpensive, and hence extremely popular white pigment [21]. TiO_2 whites **W01** - **W04** exhibit similar curves of strong backscattering and weak absorption in the visible and NIR, except for drops in backscattering around 1500 nm seen for W03 and W04. These last two samples are undiluted and 12:1 diluted versions of the same artist color. These four films demonstrate how strongly the NIR reflectance of a white film depends on film thickness—the over-black NIR reflectance of the 26 μm , 15% PVC W01 is 0.64, while that of 13- μm , 23% PVC W03 is only 0.43. The backscattering curves indicate that increased pigment loading will not necessarily improve the NIR reflectance of a thin (TiO_2) white film.

Physically, the light scattering is due to the difference between the refractive index of the rutile particles (2.7) and that of the surrounding transparent medium (1.5). At high pigment volume concentrations, the presence of numerous nearby rutile particles raises the effective refractive index of the surrounding medium, and thereby reduces the efficiency of scattering. This fall in scattering efficiency is termed pigment crowding [22].

Rutile is a direct bandgap semiconductor and therefore has a very abrupt transition from low absorption to high absorption that occurs at 400 nm, the boundary between the visible and ultraviolet regions. For wavelengths below 400 nm (photon energies above 3.1 eV), the absorption is so strong that our data saturate, except in the case of the highly dilute (2% PVC) sample W04. At wavelengths above 400 nm, absorption is weak; most of the spectral features may be attributed to the binders used. One of the three white pigments (W01) does have a slightly less abrupt transition at 400 nm—there is an absorption “tail” near the band edge. This type of behavior is likely due to impurities in the TiO_2 .

The sharp rise in absorptance near 300 nm shown for some films such as W04 is an artifact due to the use of a mylar substrate.

5.2 Black/Brown

5.2.1 Carbon Black, Other Non-Selective Black

Carbon black, bone black (10% carbon black + 84% calcium phosphate), copper chromite black ($\text{Cu Cr}_2 \text{O}_4$), and synthetic iron oxide black (Fe_3O_4 magnetite) (**B01 - B04**) are weakly scattering pigments with strong absorption across the entire solar spectrum. Carbon black B01 is the most strongly absorbing, but all three are “hot” pigments.

Most non-selective blacks are metallic in nature, with free electrons permitting many different allowed electronic transitions and therefore broad absorption spectra. Carbon black is a semi-metal that has many free electrons, but not as many as present in highly conductive metals. Both the iron oxide (magnetite) and copper chromite blacks are (electrically conducting) metals.

5.2.2 Chromium Iron Oxide Selective Black

Chromium iron oxide selective blacks (**B05 - B11**) are mixed metal oxides (chromium green-black hematite, chromium green-black hematite modified, chromium iron oxide, or chromium iron nickel black spinel) formulated to have NIR reflectance significantly higher than carbon and other non-selective blacks. Some, such as chromium green-black hematite B06, appear more brown than black. While these pigments have good scattering in the NIR, with a backscattering coefficient at 1000 nm about half that of TiO_2 white, they are also quite absorbing ($K \approx 50 \text{ mm}^{-1}$) in the short NIR. These pigments are visibly hiding (opaque to visible radiation) and NIR transmitting, so use of a white background improves their NIR reflectances without significantly changing their appearances.

Pure chromium oxide green (Cr_2O_3), pigment green 17, has the hematite crystal structure and will be discussed further together with other green pigments. When some of the chromium atoms are replaced by iron, a dark brownish black with the same crystal structure is obtained—i.e., a traditional cool black pigment (e.g., B06-B11; B05 differs because it contains nickel and has a spinel structure). It is sometimes designated as Cr-Fe hematite [23] or chromium green-black hematite [24], and has been used to formulate infrared-reflective vinyl siding since about 1984 [25]. A number of modern recipes for modified versions of this basic cool black incorporate minor amounts of a variety of other metal oxides. One example is the use of a mixture of 93.5 g of chromium oxide, 0.94

g of iron oxide, 2.38 g of aluminum oxide, and 1.88 g of titanium oxide [3]. The mixture is calcined at about 1100°C to form hematite-structure crystallites of the resulting mixed metal oxide.

5.2.3 Organic Selective Black

Perylene black (**B12**) is a weakly scattering, dyelike organic pigment that absorbs strongly in the visible and very weakly in the NIR. Its sharp absorption decrease at 700 nm gives this pigment a jet black appearance and an exceptionally high NIR reflectance (0.85) when applied over white. Perylene pigments exhibit excellent lightfastness and weatherfastness, but their basic compound (dianhydride of tetracarboxylic acid) may or may not be fast to alkali; references [26] and [21] disagree on the latter point

5.2.4 Iron Oxide Brown

Iron oxide browns (**B13 - B15**) such as burnt sienna, raw sienna, and raw umber exhibit strong absorption in part of the visible spectrum and low absorption in the NIR. These can provide effective cool brown coatings if given a white background, though this will make some (e.g., burnt sienna B13) appear reddish. These browns are “natural” and can be expected to contain various impurities.

5.2.5 Other Brown

Other browns characterized (**B16 - B21**) include iron titanium (Fe-Ti) brown spinel, manganese antimony titanium buff rutile, and zinc iron chromite brown spinel. These mixed-metal oxides have strong absorption in most or all of the visible spectrum, plus weak absorption and modest scattering in the NIR. A white undercoating improves the NIR reflectance of all browns, but brings out red tones in iron titanium brown spinels B16 and B17.

The cool Fe-Ti browns (B16 - B18) have spinel crystal structure and basic formula Fe_2TiO_4 [24, 27]. Despite the presence of Fe^{2+} ions, the infrared absorption of this material is weak. (In many materials, the Fe^{2+} ion is associated with infrared absorption [28, 29]; see also our data for Fe_3O_4 . The current data demonstrate that the absorption spectra also depend on the environment of the Fe^{2+} ion.) We also note that while B17 and B18 are nominally the same material, the details of the absorption are different.

We have not yet characterized a synthetic iron oxide hydrate brown (e.g., FeOOH).

5.3 Blue/Purple

5.3.1 Cobalt Aluminate Blue, Cobalt Chromite Blue

Cobalt aluminate blue (nominally CoAl_2O_4 , but usually deficient in Co [30]; **U01** - **U05**) and cobalt chromite blue ($\text{Co}[\text{Al,Cr}]_2\text{O}_4$; **U06** - **U09**) derive their appearances from modest scattering ($S \approx 30 \text{ mm}^{-1}$) in the blue (400 - 500 nm) and strong absorption ($K \approx 150 \text{ mm}^{-1}$) in rest of the visible spectrum. They have very low absorption in the short NIR, but exhibit an undesirable absorption band in 1200 - 1600 nm range, which contains 17% of the NIR energy. A white background dramatically increases NIR reflectance but makes some (e.g., cobalt aluminum blue spinel U02) much lighter in color.

5.3.2 Iron Blue

Iron (a.k.a. Prussian or Milori) blue (**U10**) is a weakly scattering pigment with strong absorption in the visible and short NIR, and weak absorption at longer wavelengths. It appears black and has little NIR reflectance over a black background, but looks blue and has achieves a modest NIR reflectance (0.25) over a white background. It is not ideal for cool coating formulation.

5.3.3 Ultramarine Blue

Ultramarine blue (**U11**), a complex silicate of sodium and aluminum with sulfur, is a weakly scattering pigment with some absorption in the short NIR. If sparingly used, it can impart absorption in the yellow spectral region without introducing a great deal of NIR absorption. This is a durable inorganic pigment with some sensitivity to acid [21].

While most colored inorganic pigments contain a transition metal such as Fe, Cr, Ni, Mn, and Co, ultramarine blue is unusual. It is a mixed oxide of Na, Si, and Al, with a small amount of sulfur ($\text{Na}_{7.5}\text{Si}_6\text{Al}_6\text{O}_{24}\text{S}_{4.5}$). The metal oxide skeleton forms an open clathrate sodalite structure that stabilizes S_3^- ions in cages to form the chromophores [30, section 3.5] [31]. Thus isolated S_3 molecules with an attached unpaired electron cause the light absorption in the 500-700 nm range, producing the blue color. The refractive index of ultramarine blue is not very different from the

typical matrix value of 1.5 [30, section 3.5], so the pigment causes little scattering.

5.3.4 Phthalocyanine Blue

Copper phthalocyanine blue (**U12** - **U13**) is a weakly scattering, dyelike pigment with strong absorption in the 500 - 800 nm range and weak absorption in the rest of the visible and NIR. Phthalo blue appears black and has minimal NIR reflectance over a black background, but looks blue and achieves a high NIR reflectance (0.63) over a white background (U12). It is durable and lightfast, but as an organic pigment it is less chemically stable than (high temperature) calcined mixed metal oxides such as the cobalt aluminates and chromites. General information on the structure and properties of phthalocyanines is available in [32]. The refractive index varies with wavelength, and exceeds 2 in the short wavelength part of the infrared spectrum [33]. Therefore the weak scattering we observe in our samples indicates that the particle size is quite small. The pigment handbook indicates a typical particle diameter of 120 nm [21], which is consistent with our data.

5.3.5 Dioxazine Purple

Dioxazine purple (**U14**) is an organic optically similar to phthalo blue, but even more absorbing in the visible and less absorbing in the NIR. It is nearly ideal for formulation of dark NIR-transparent layers, but is subject to the chemical stability considerations noted above for phthalo blue.

5.4 Green

5.4.1 Chromium Oxide Green, Modified Chromium Oxide Green

Chromium oxide green Cr_2O_3 (**G01** - **G02**) exhibits strong scattering alternating with strong absorption across the visible spectrum, and strong scattering and mild absorption in the NIR. Since the pigment is almost opaque in the visible, a thin layer of chromium oxide green over a white background yields a medium-green coating with good NIR reflectance (0.57 for 12- μm thick film G02). The modified chromium oxide green (**G03**) is mostly chromium oxide, with small amounts of iron oxide, titanium dioxide, and aluminum oxide [3]. A layer of the modified chromium oxide green over a white background produces a medium green with excellent NIR reflectance (0.71).

Cr_2O_3 green is often mentioned as an infrared-reflective pigment that is useful for simulating the high infrared reflectance of chlorophyll in plant leaves. Indeed, a high IR reflectance is observed. However, our data for sample films G01 and G02 do show that there is a broadband absorption of about 10 mm^{-1} in the infrared. While our measurements of absorptance coefficient are not precise for low absorptances, this value is clearly distinct from zero. Pure Cr_2O_3 , fired in air, tends to become slightly rich in oxygen, which results in p-type semiconducting behavior [34, 35]. Thus it is possible that the broadband IR absorption of Cr_2O_3 is due to free carrier absorption by mobile holes. Ref. [34] also reports that doping with Al can reduce the p-type conductivity in Cr_2O_3 , so it seems likely that doping with Al and/or certain other metals can also reduce the IR absorption.

The modified chromium oxide green G03 is similar to G01 and G02 Cr_2O_3 . However its green reflectance peak at 550 nm is somewhat smaller and its infrared absorption is clearly much smaller than those of samples G01 and G02.

5.4.2 Cobalt Chromite Green

Cobalt chromite green (**G04 - G06**) is similar to cobalt chromite blue, and is commonly used for military camouflage.

5.4.3 Cobalt Titanate Green

Cobalt titanate green (**G07 - G09**) is similar to cobalt chromite green, but scatters more strongly across the entire solar spectrum and has a pronounced absorption trough around 500 nm. A white background makes cobalt teal G07 very NIR reflective (0.72) but also appear light blue (hence, the name teal). The other two cobalt titanate greens (G08, G09) have respectable NIR reflectances (0.47, 0.37) over white and appear medium green.

5.4.4 Phthalocyanine Green

Phthalocyanine green (**G10 - G11**) is similar to phthalocyanine blue, but absorbs more strongly in the short NIR. Hence, the NIR reflectance of a thin phthalo green film over white (G04), while respectable, is only 70% of that achieved by a thin layer of phthalo blue over white (0.45 vs. 0.63). Note also that the error in predicted reflectance over white for G05 is large [18].

5.5 Red/Orange

5.5.1 Iron Oxide Red

Iron oxide red (**R01 - R04**) derives its appearance from weak scattering and very strong absorption in the 400 - 600 nm band. One of the iron oxide reds (R01) exhibits moderate absorption across the NIR that may be due to doping of the Fe_2O_3 hematite crystals with impurities or result from broadband absorbing impurity phases such as Fe_3O_4 ; it is not a cool pigment. However, the remaining three iron oxide reds weakly absorb in the NIR and present both a dark red appearance and good NIR reflectance (0.53 - 0.67) over a white background. R02 also has a respectable NIR reflectance (0.38) over a black background, and has backscattering S comparable with TiO_2 white in the NIR.

5.5.2 Cadmium Orange

Cadmium orange (**R05**) has weak scattering and very strong absorption in the 400 - 600 nm band, followed by strong scattering and virtually no absorption at longer wavelengths. Applied over a white background, it appears bright orange and has very high NIR reflectance (0.87)—essentially the same as that of the white background. Cadmium orange (and cadmium yellow, below) are $\text{Cd}(\text{S},\text{Se})$ direct bandgap semiconductors. They exhibit sharp transitions between absorbing and non-absorbing regions, and have high refractive indices (e.g., 2.5 for CdS) that lead to large scattering coefficients. However, the toxicity of cadmium and sensitivity to acid limits their applications.

5.5.3 Organic Red

Organic red pigments (**R06 - R09**) such as acra burnt orange, acra red, monastral red, and naphthol red light have weak scattering and strong (sometimes very strong) absorption up to 600 nm, followed by very weak absorption and moderate-to-weak scattering at longer wavelengths. As a result they yield a medium-red color and a very high NIR reflectance (0.82 - 0.87) when applied over a white background. Mastones of acra burnt orange, acra red, and naphthol red light are all lightfast; their tints are slightly less so [21].

5.6 Yellow

5.6.1 Iron Oxide Yellow

Iron oxide yellow FeOOH (**Y01**) is a brownish yellow similar to iron oxide red. It appears tan and has a high NIR reflectance (0.70) when applied over a white background.

5.6.2 Cadmium Yellow

Cadmium yellow (**Y02**) is similar to cadmium orange. It appears bright yellow and has very high NIR reflectance (0.87) over white.

5.6.3 Chrome Yellow

Chrome yellow PbCrO_4 (**Y03**) is optically similar to cadmium yellow but exhibits a more gradual reduction in absorptance. It appears bright yellow and achieves a high NIR reflectance (0.82) over white. In some applications, the presence of lead and/or the Cr(VI) ion impose limitations.

5.6.4 Chrome Titanate Yellow

Chrome titanate yellow (**Y04 - Y07**) is similar to chrome yellow, but scatters more strongly in the NIR. Its scattering coefficient can exceed 100 mm^{-1} in the short NIR, suggesting that this pigment might be used in place of titanium white to provide a background of high NIR reflectance. Over a black background, chrome titanate yellow appears brown to green and has moderate to high NIR reflectance (0.26 - 0.62). Over white, it appears orange to yellow and has very high NIR reflectance (0.80 - 0.86). Y07 over black produces a medium brown with NIR reflectance 0.62.

The data for Y04 and Y05 illustrate how the scattering coefficient S varies with particle size (manufacturer data). For smaller particles, the decrease in S with increasing wavelength is more dramatic.

5.6.5 Nickel Titanate Yellow

Nickel titanate yellow (**Y08 - Y11**) is similar to chrome titanate yellow. Note that these compounds usually also contain antimony in their formulation. Over white, it appears a muted yellow and yields

very high NIR reflectance (0.77-0.85); over black, it appears yellowish green and achieves high NIR reflectance (0.42 - 0.64). Y11 is a particularly good candidate to use over black.

5.6.6 Strontium Chromate Yellow + Titanium Dioxide

Strontium chromate yellow (solids mass fraction 11%) mixed with titanium dioxide (solids mass fraction 9%) in a paint primer (**Y12**) appears greenish brown over a black background, and pale yellow over a white background. It has very low absorption (order 1 mm^{-1}) and strong scattering (order 100 mm^{-1}) at 1000 nm, giving it a good NIR reflectance over black (0.38) and a very high NIR reflectance over white (0.86).

5.6.7 Hansa Yellow, Diarylide Yellow

Hansa yellow (**Y13**) and diarylide yellow (**Y14**) are weakly scattering, dyelike organic pigments with high absorption below 500 nm and very weak absorption elsewhere. Over white, they appear bright yellow and orange-yellow, respectively, and yield very high NIR reflectance (0.87).

5.7 Pearlescents

5.7.1 Mica + Titanium Dioxide

Mica flakes coated with titanium dioxide (**P01** - **P09**) exhibit strong scattering and weak absorption, producing their colors (e.g., gold, blue, green, orange, red, violet, or bright white) via thin-film interference. Some have scattering coefficients exceeding 100 mm^{-1} in the near infrared. Over white, they appear white and have very high NIR reflectance (0.88 - 0.90); over black, they achieve their named colors and have high NIR reflectance (0.35 - 0.54). The NIR reflectance of a pearlescent film over an opaque white background can exceed that of the background.

5.7.2 Mica + Titanium Dioxide + Iron Oxide

Mica flakes coated with titanium dioxide and iron oxide (**P10** - **P14**) are in most cases similar to mica flakes coated with only titanium dioxide, but are more absorbing, less scattering, darker, and somewhat less reflecting in the NIR. The exception is rich bronze P10, which has very high absorption and would not make a suitable cool pigment.

5.8 Aluminum + Iron Oxide + Silicon Oxide

While not characterized in the current study, the solar spectral reflectances of single-layer (iron oxide Fe_2O_3) or double layer (Fe_2O_3 on silicon dioxide SiO_2) interference coatings on aluminum flakes are presented in Refs. [36, 37].

5.9 Cool and Hot Pigments

A simple way to evaluate the utility of a coating for “cool” applications is to consider its NIR absorptance and NIR transmittance. If the NIR absorptance is low, the pigment is cool. However, a cool pigment that has high NIR transmittance will require an NIR-reflective background (typically white or metallic) to produce an NIR-reflecting coating. Charts of the NIR absorptance and transmittance of the members of each color family are shown in Fig. 2. An ideal cool pigment would appear near the lower left corner of the chart, indicating that it is weakly absorbing, weakly transmitting, and thus strongly reflecting in the NIR. Pigments appearing higher on the left side of the chart will form a cool coating if given an NIR-reflective background. Use of pigments appearing toward the right side of the chart (i.e., those with strong NIR absorption) should be avoided in cool applications. It should be noted that these charts do not provide perfect comparisons of “cool” performance because they show the NIR properties of films of varying thickness (10 - 37 μm) and visible hiding (visible transmittance 0 - 0.43 for non-pearlescents, and 0.02 - 0.54 for the pearlescents). Black-filled circles indicate visible transmittance less than 0.1; gray-filled circles, between 0.1 and 0.3; and white-filled circles, above 0.3.

There are cool films in the white, yellow, brown/black, red/orange, blue/purple, and pearlescent families with NIR absorptance less than 0.1. These films have moderate to high NIR transmittance (0.25 - 0.85), indicating that they would require an NIR-reflective background to perform well. There are also other slightly less cool black/brown, blue/purple, green, red/orange, yellow and pearlescent films with NIR absorptance less than 0.2. These have somewhat lower NIR transmittances (0.20 - 0.70), but are still far from NIR-opaque. A handful of pearlescent, blue/purple, green and red/orange films, along with half a dozen brown/black films, have NIR absorptances exceeding 0.5 and may be considered warm. A few nonselective blacks with NIR absorptance approaching unity may be considered hot.

Other useful metrics for “coolness” are NIR reflectances over white and black backgrounds (Table 1). Over a white background, the coolest pigments—i.e., those with NIR reflectances of at least 0.7—include members of the pearlescent, white, yellow, black/brown, red/orange, and blue/purple color families: mica coated w/titanium dioxide (0.88-0.90), titanium dioxide white (0.87), cadmium yellow (0.87), cadmium orange (0.87), Hansa yellow (0.87), diarylide yellow (0.87), organic selective black (0.85), organic red (0.83-0.87), dioxazine purple (0.82), chrome titanate yellow (0.80-0.86), nickel titanate yellow (0.77-0.85), modified chromium oxide green (0.71), and iron oxide yellow (0.70). Other pigments with NIR reflectances of at least 0.5 include members of the blue/purple, black/brown, and green color families: cobalt aluminum blue (0.61-0.70), cobalt chromite blue (0.54-0.70), phthalo blue (0.55-0.63), cobalt chromite green (0.58-0.64), ultramarine blue (0.52), chromium oxide green (0.50-0.57), and other brown (0.50-0.74). Over a black background, the coolest pigments—in this case, those with NIR reflectances of at least 0.3—include members of the white, yellow, pearlescent, and green color families: titanium dioxide white (0.43-0.65), nickel titanate yellow (0.42-0.64), mica coated w/titanium dioxide (0.31-0.54), and chromium oxide green (0.33-0.40).

6 Conclusions

Our characterizations of the solar spectral optical properties of 87 predominately single-pigment paint films with thicknesses ranging from 10 to 37 μm have identified cool pigments in the white, yellow, brown/black, red/orange, blue/purple, and pearlescent color groupings with NIR absorptances less than 0.1, as well as other pigments in the black/brown, blue/purple, green, red/orange, yellow and pearlescent groupings with NIR absorptances less than 0.2. Most are NIR transmitting and require an NIR-reflecting background to form a cool coating. Over an opaque white background, some pigments in the pearlescent, white, yellow, red/orange, green, and blue/purple families offer NIR reflectances of at least 0.7, while other pigments in the blue/purple, black/brown, and green color families have NIR reflectances of at least 0.5. A few members of the white, yellow, pearlescent, and green color families have NIR scattering sufficiently strong to yield NIR reflectances of at least 0.3 (and up to 0.64) over a black background.

Use of pigments with NIR absorptances approaching unity (e.g., nonselective blacks) should

be minimized in cool coatings, as might be the use of certain pearlescent, blue/purple, green and red/orange, and brown/black pigments with NIR absorptances exceeding 0.5.

Acknowledgements

This work was supported by the California Energy Commission (CEC) through its Public Interest Energy Research Program (PIER), by the Laboratory Directed Research and Development (LDRD) program at Lawrence Berkeley National Laboratory (LBNL), and by the Assistant Secretary for Renewable Energy under Contract No. DE-AC03-76SF00098. The authors wish to thank CEC Commissioner Arthur Rosenfeld and PIER program project managers Nancy Jenkins and Chris Scruton for their support and advice. Special thanks go also to Mark Levine, director of the Environmental Energy Technologies Division at LBNL, and Stephen Wiel, head of the Energy Analysis Department at LBNL, for their encouragement and support in the initiation of this project. We also wish to thank the following people for their assistance: Kevin Stone and Melvin Pomerantz, LBNL; Michelle Vondran, John Buchko, and Robert Scichili, BASF Corporation; Richard Abrams, Robert Blonski, Ivan Joyce, Ken Loye, and Ray Wing, Ferro Corporation; Tom Steger and Jeffrey Nixon, Shepherd Color Company; and Robert Anderson, Liquitex Artist Materials.

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Category	ROW _{nir}	ROB _{nir}	T _{vis}	$\delta(\mu\text{m})$	Film Codes
titanium dioxide white	0.87-0.88	0.24-0.65	0.10-0.42	12-29	W01-W04
carbon black	0.06-0.06	0.04-0.04	0.05-0.07	16-21	B01-B02
other non-selective black	0.04-0.05	0.04-0.05	0.00-0.07	20-24	B03-B04
chromium iron oxide selective black	0.23-0.48	0.11-0.35	0.00-0.15	19-26	B05-B11
organic selective black	0.85	0.10	0.01	23	B12
iron oxide brown	0.47-0.61	0.06-0.27	0.03-0.24	14-26	B13-B15
other brown	0.50-0.74	0.22-0.40	0.01-0.24	17-28	B16-B21
cobalt aluminate blue	0.62-0.71	0.09-0.20	0.16-0.28	16-23	U01-U05
cobalt chromite blue	0.55-0.70	0.10-0.25	0.05-0.28	16-26	U06-U09
Prussian blue	0.25	0.05	0.27	12	U10
ultramarine blue	0.52	0.05	0.20	23	U11
phthalocyanine blue	0.55-0.63	0.06-0.08	0.21-0.22	14-26	U12-U13
dioxazine purple	0.82	0.05	0.21	10	U14
chromium oxide green	0.50-0.57	0.33-0.40	0.00-0.01	12-26	G01-G02
modified chromium oxide green	0.71	0.22	0.22	23	G03
cobalt chromite green	0.58-0.64	0.14-0.18	0.17-0.28	13-23	G04-G06
cobalt titanate green	0.37-0.73	0.21-0.30	0.04-0.22	10-24	G07-G09
phthalocyanine green	0.42-0.45	0.06-0.07	0.10-0.20	13-25	G10-G11
iron oxide red	0.31-0.67	0.19-0.38	0.00-0.08	13-26	R01-R04
cadmium orange	0.87	0.26	0.18	10	R05
organic red	0.83-0.87	0.06-0.14	0.15-0.32	11-27	R06-R09
iron oxide yellow	0.70	0.21	0.16	19	Y01
cadmium yellow	0.87	0.29	0.25	11	Y02
chrome yellow	0.83	0.34	0.18	24	Y03
chrome titanate yellow	0.80-0.86	0.26-0.62	0.05-0.23	17-26	Y04-Y07
nickel titanate yellow	0.77-0.85	0.42-0.64	0.09-0.29	17-27	Y08-Y11
strontium chromate yellow + titanium dioxide	0.86	0.38	0.21	19	Y12
Hansa yellow	0.87	0.06	0.43	11	Y13
diarylide yellow	0.87	0.08	0.35	12	Y14
mica + titanium dioxide	0.88-0.90	0.35-0.54	0.31-0.54	17-37	P01-P09
mica + titanium dioxide + iron oxide	0.27-0.85	0.25-0.44	0.02-0.42	20-24	P10-P14

Table 1: Ranges of NIR reflectance over white (ROW_{nir}), NIR reflectance over black (ROW_{nir}), visible transmittance (T_{vis}), and thickness (δ) measured for pigmented films in each pigment category.

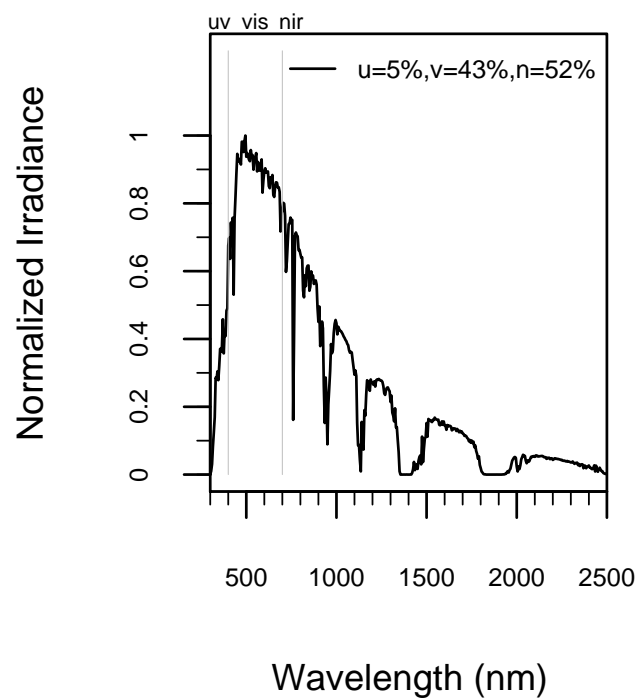


Figure 1: Air mass 1.5 hemispherical solar spectral irradiance typical of North American insolation (5% ultraviolet, 43% visible, 52% near-infrared) [10].

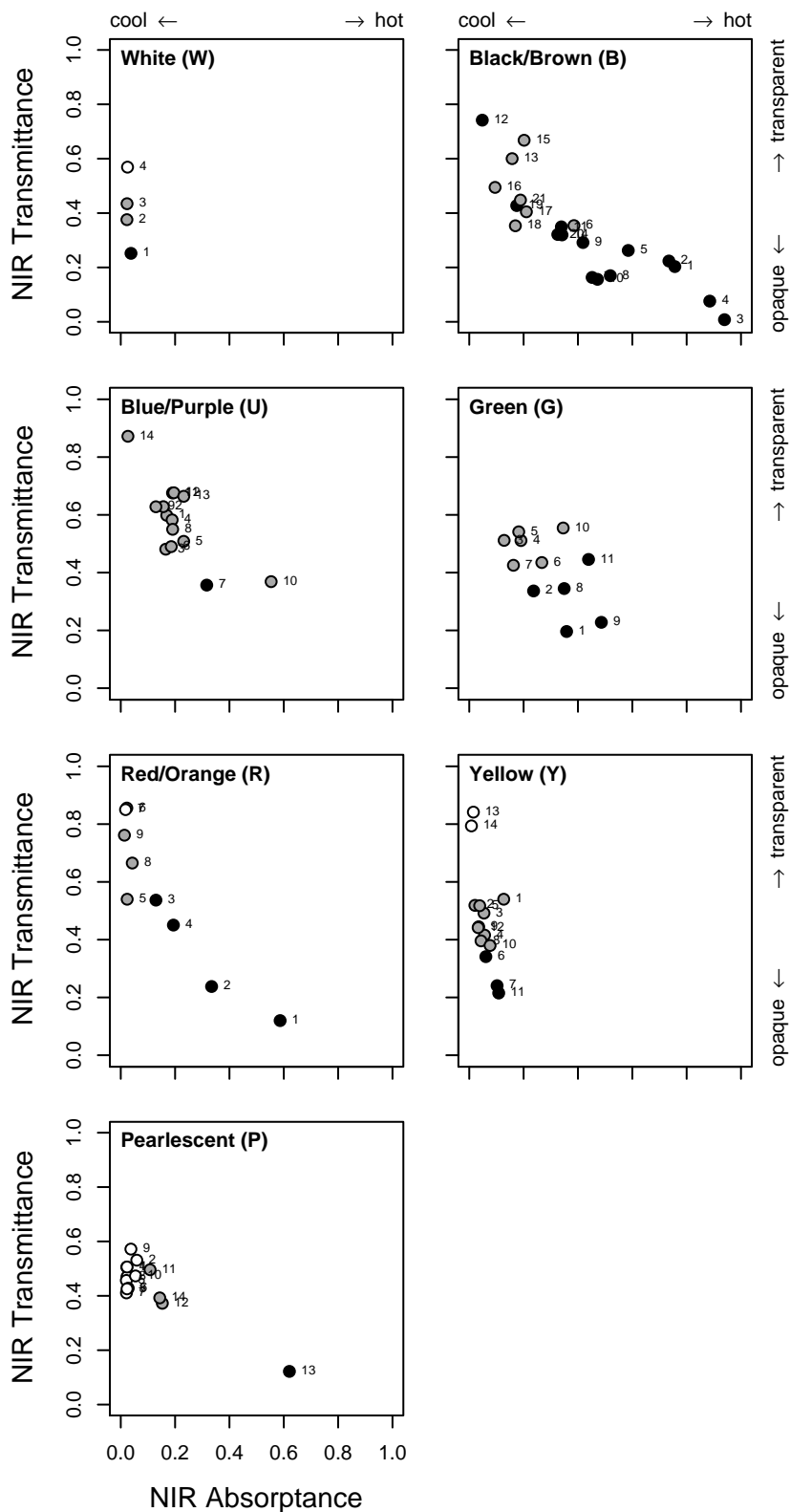


Figure 2: NIR absorbances and transmittances of 87 pigmented films. A pigment with low NIR-absorbance is cool, but a cool pigment with high NIR transmittance requires an NIR-reflecting background. The color of each circle's interior indicates visible transmittance: black, less than 0.1; gray, between 0.1 and 0.3; white, over 0.3.