Cool Colors for Summer

Characterizing the Radiative Properties of Pigments for Cool Roofs

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Presentation Overview

I. Introduction to cool colored roofs

II. Characterizing the *solar spectral* radiative properties of pigments

III. Identifying cool and hot pigments

Part I

Introduction to Cool Colored Roofs

Cool Roof Technologies

Old

flat, white

pitched, white

New

pitched, cool & colored

Cool Roof Benefits

- For buildings
  - Reduce air conditioning energy use ~ 10%
  - Cool interior of unconditioned homes
  - May last longer (less thermal stress)
- For cities with many cool roofs
  - Can lower outside air temperature ~ 1-2 °C
  - Reduces smog

Radiative Properties of a Cool Roof Surface

- High solar reflectance (white, cool color, shiny metal)
  - Ability to reflect sunlight (0.3-2.5 μm)
  - High solar reflectance *prevents* solar heat gain
- High thermal emittance (not a bare metal)
  - Ability to radiate heat (~10 μm)
  - High thermal emittance *dissipates* solar heat gain
- **Our focus: high solar reflectance for colored surfaces**

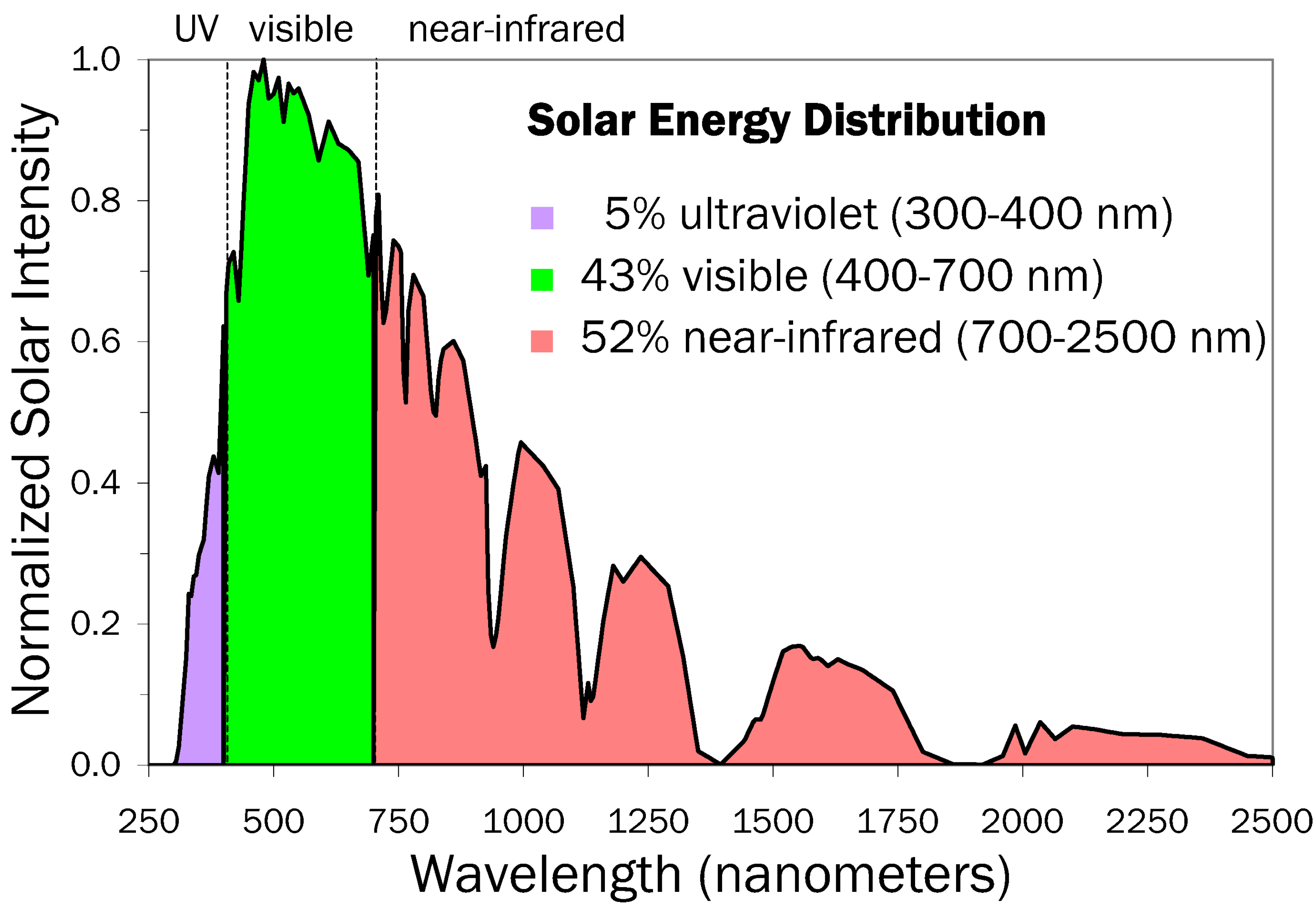
Need for Cool Colors

- White roofs are very cool...
  - Initial solar reflectance > 0.7
  - Ideal for roofs out of view

...but many homeowners prefer nonwhite roofs

- Cool colored roofs
  - Match standard colors
  - Reflect more *invisible* sunlight (near-infrared)

Cool Colors Reflect Invisible Near-Infrared Sunlight

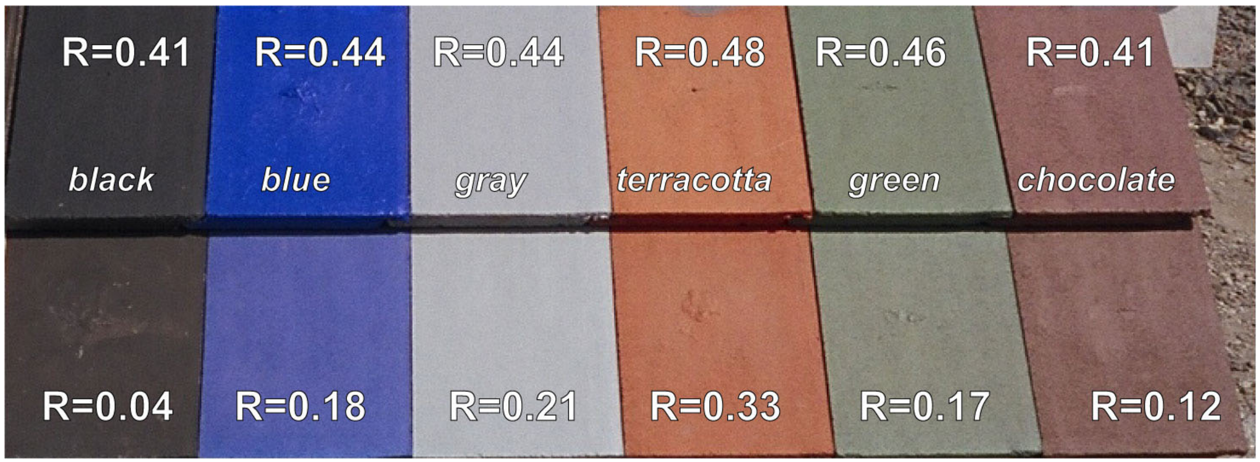


Increasing Solar Reflectance Using Cool Colors

- 52% of sunlight is near-infrared (NIR) radiation
- Standard colors
  - Light colors have high visible, NIR reflectances
  - Dark colors have low visible, NIR reflectances
- Cool colors
  - **Have high NIR reflectance**
  - Visible reflectance depends on color
  - Increasing NIR reflectance from 0 to 1 raises *solar* reflectance by about 0.5
  - Solar reflectance gains greatest for dark colors
    - Low initial NIR reflectance

Example 1: Cool and Standard Color-Matched Concrete Tiles

Courtesy American Rooftile Coatings



cool

standard

ΔR=0.37 ΔR=0.26 ΔR=0.23 ΔR=0.15 ΔR=0.29 ΔR=0.29

- Solar reflectance gains typically about 0.3
- Gains greatest for dark colors

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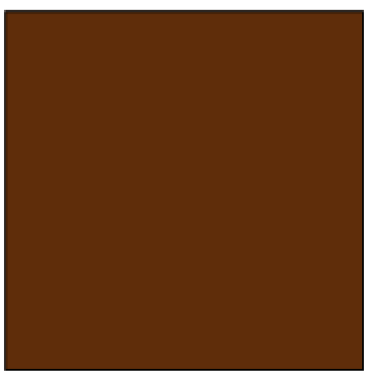
Example 2: Cool and Standard Brown Metal Roofing Panels

- Solar reflectance ~ 0.2 higher
- Afternoon surface temperature ~ 10ºC lower

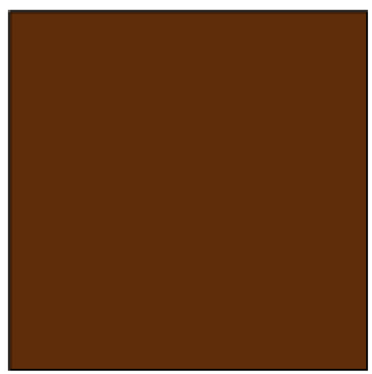
Courtesy BASF Coatings

cool

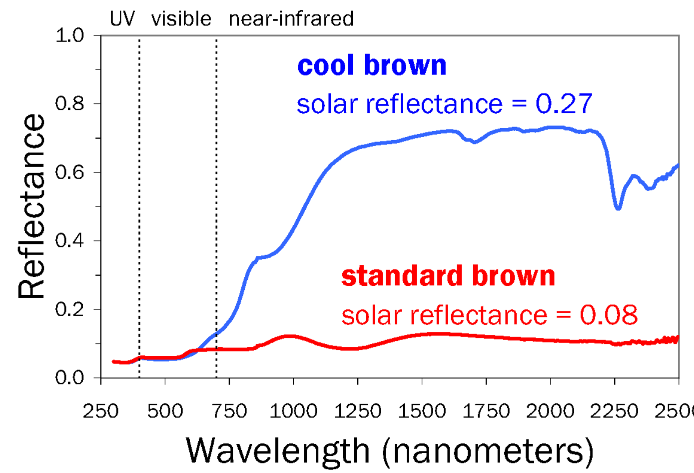


solar reflectance = 0.27
thermal emittance = 0.85
roof temp – air temp = 36ºC (65ºF)

standard



solar reflectance = 0.08
thermal emittance = 0.85
roof temp – air temp = 45ºC (81ºF)

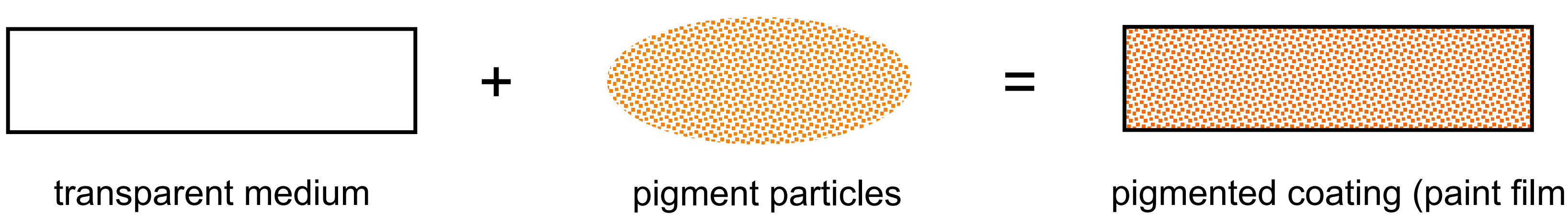


Part II

Characterizing the Solar Spectral Radiative Properties of Pigments

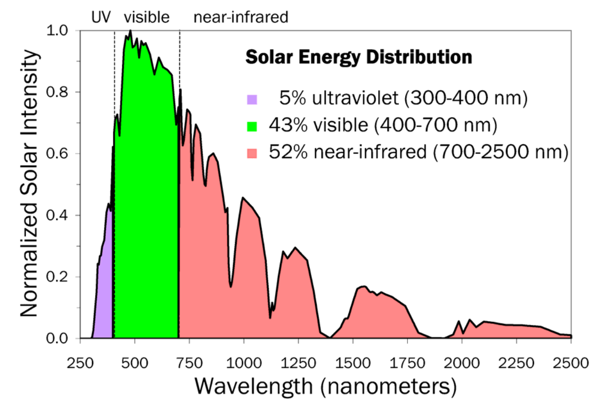
Our Cool Pigment Research

- Objective
  - Improve solar reflectance of architectural coatings by identifying cool and hot pigments
- Approach: investigate **solar spectral** properties
  - Reflectance, transmittance, absorptance of paint films
  - Scattering, absorption by pigments in transparent media



Near-Infrared Absorption

- Near-infrared (NIR) radiation
  - Invisible
  - 0.7 - 2.5 µm
  - 52% of sunlight



- Absorption converts light to heat
  - Strong NIR absorption → hot pigment
  - Weak NIR absorption → cool pigment

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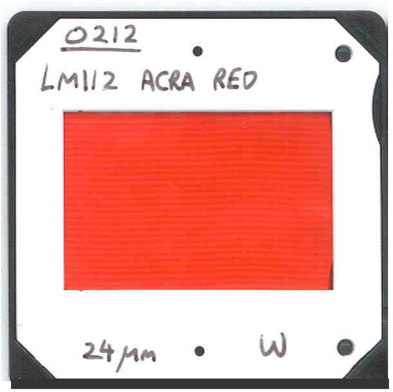
Cool Pigments Scatter and/or Transmit NIR Radiation

- Scattering (backscattering) reflects radiation
- Some cool pigments strongly scatter NIR light
  - Classified as *NIR-scattering* cool pigments
  - Produce cool coatings over any background
- Other cool pigments weakly scatter NIR light
  - Classified as *NIR-transmitting* cool pigments
  - Produce cool coatings over NIR-reflective backgrounds

Preparing Paint Film (Pigment in Transparent Medium)

- Create thin pigmented film (~ 25 μm)
  - Polyvinylidene fluoride (PVDF) resin paint (no substrate)
  - Acrylic resin paint (clear polyester substrate)
- Cut out 3 samples; measure thicknesses
- Undercoat 2 samples, leaving 3rd as free film

acra red over opaque white



front

back

acra red over opaque black

front

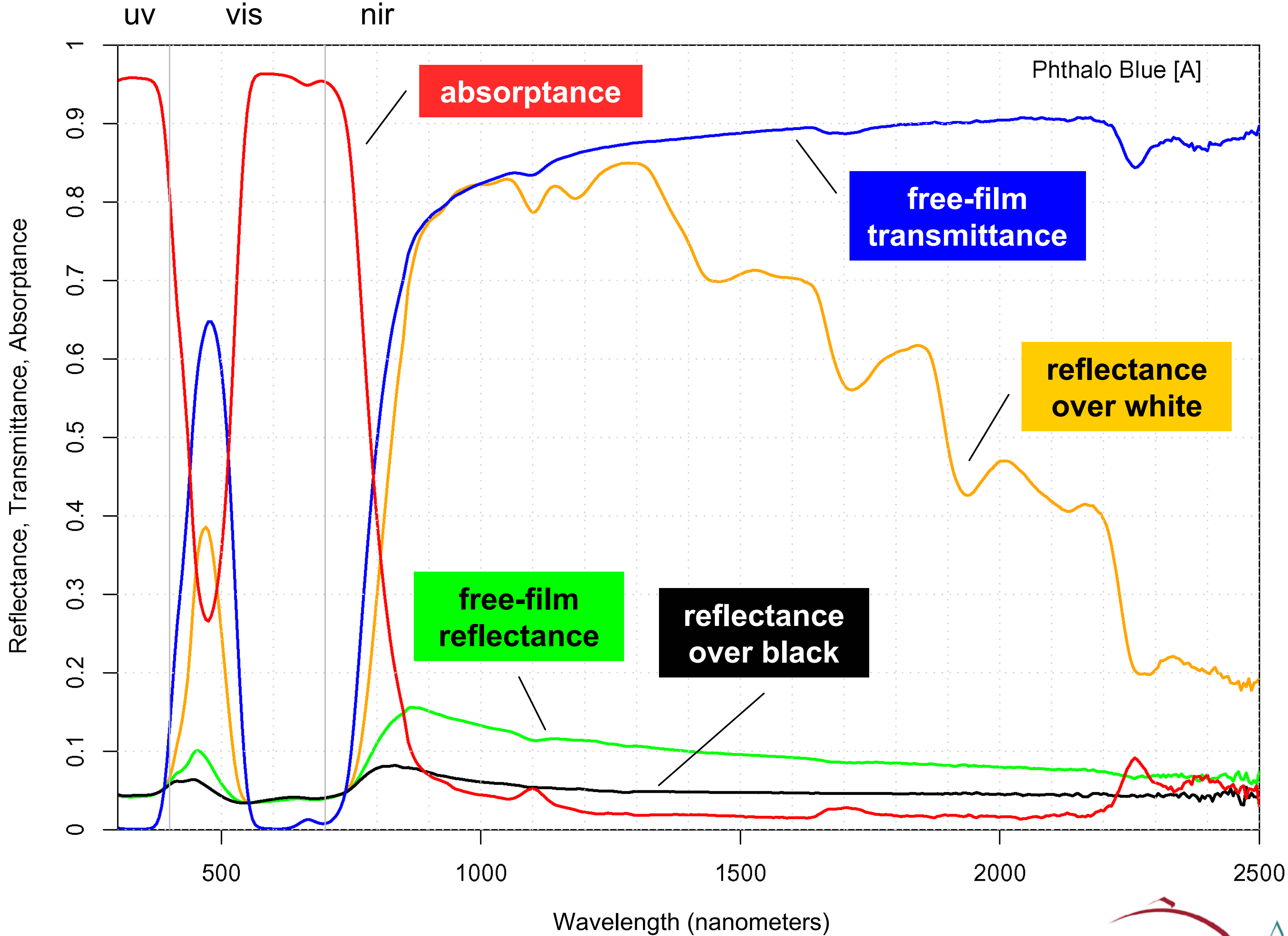
back

Measuring Solar Spectral Properties of Pigmented Film

- Four solar spectral measurements
  - Transmittance (T) of free film
  - Reflectance (R) of free film
  - Reflectance of film over opaque black
    - *Minimum* possible reflectance
  - Reflectance of film over opaque white
    - *Maximum* possible reflectance (approximately)
- Measurements span 300 - 2,500 nm @ 5 nm

Absorptance
($A=1-R-T$)

Sample Film Measurements



Estimating Absorption, Scattering Via Empirical Continuum Model

- Treat pigmented film as continuum
- Reflectance, transmittance ↔ scattering, absorption
- Simple model (e.g., Kubelka-Munk)
  - Assumes perfectly diffuse light
  - Describes pigment with just 2 spectral parameters
  - Simple closed-form solutions
- Complex model (e.g., Maheu-Letoulouzan-Gouesbet)
  - Relaxes assumption of perfectly diffuse light
  - Uses at least 4 spectral parameters to describe pigment
  - Unwieldy closed-form solutions

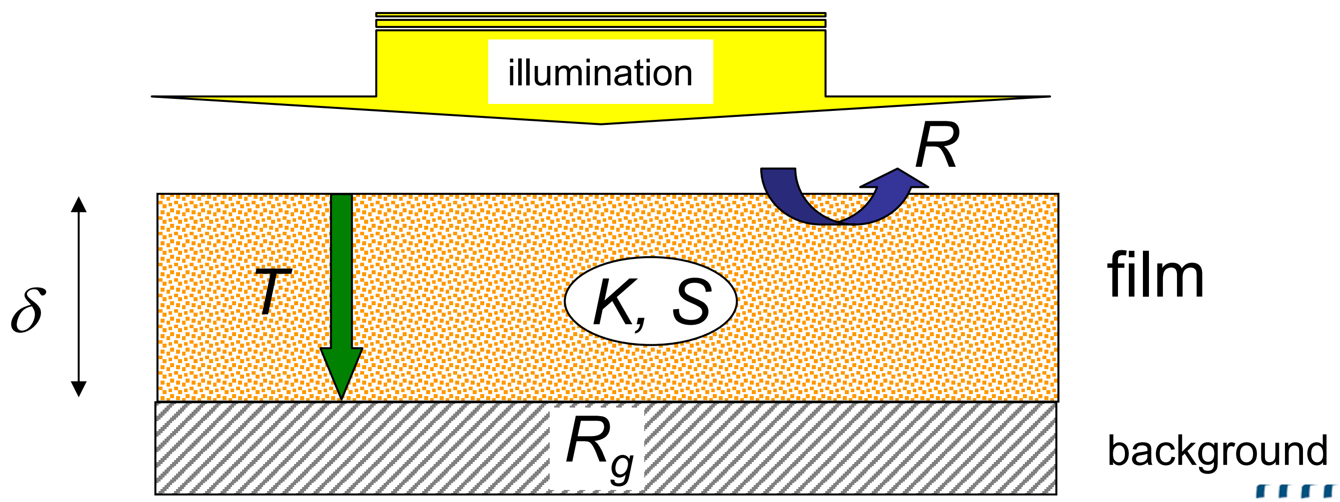
Simplest Continuum Model: Kubelka-Munk (K-M) Two-Flux

Relates pigmented-film properties...

- reflectance (R), transmittance (T), thickness (δ), background reflectance (R_g)

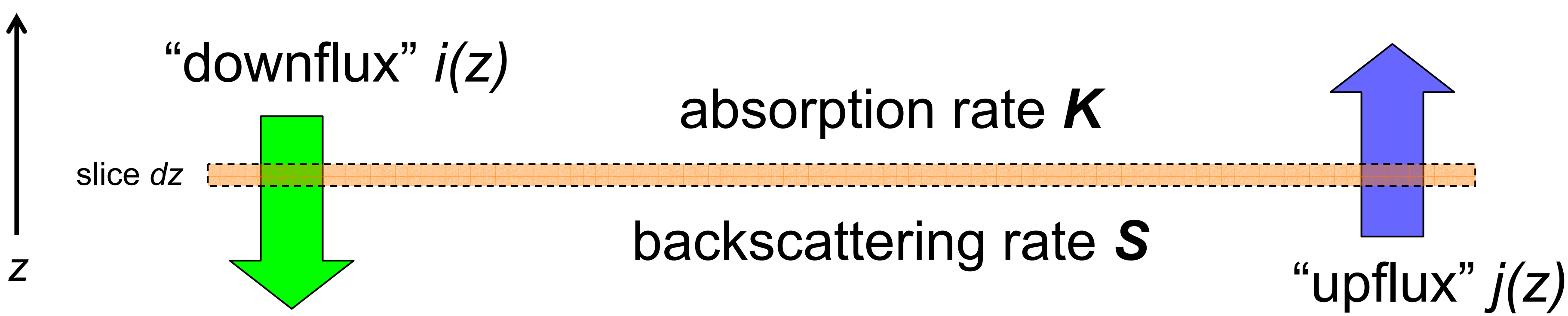
...to properties of pigment (in transparent medium)

- absorption coefficient (K), backscattering coefficient (S)



Physical Description of Standard K-M Two-Flux Model

- Film diffusely illuminated from above
- Downward and upward light fluxes $i(z)$, $j(z)$
- Fluxes can be partially absorbed or backscattered while traversing a thin slice of the film (dz)
- Backscattering transfers light to opposite flux ($i \leftrightarrow j$)
- Each wavelength of light considered independently
- **Describes only light inside film (excludes air/film interfaces)**



Mathematical Description of Standard K-M Two-Flux Model

- Two coupled ordinary differential equations

$-di/dz = -(K + S)\, i + S\, j$	downflux rate of change
$dj/dz = -(K + S)\, j + S\, i$	upflux rate of change

- Boundary conditions
  - Unit diffuse illumination at film top
  - Background of reflectance R_g at film bottom
- Hyperbolic closed-form solutions
  - Film properties $\{R, T, R_g, \delta\} \leftrightarrow$ pigment properties $\{K, S\}$

K-M Solutions Are Simple...

Pigment props → film props

$$R_f \equiv \left(\frac{j}{i}\right)_{z=\delta} = \frac{1 - R_g(a - b\coth bS\delta)}{a - R_g + b\coth bS\delta}$$

$$\begin{aligned} a &\equiv (S+K)/S \\ b &\equiv (a^2-1)^{\frac{1}{2}} \end{aligned}$$

$$\tau \equiv \frac{i_{z=0}}{i_{z=\delta}} = \frac{b}{a\sinh bS\delta + b\cosh bS\delta}$$

Film props → pigment props

$$S = \frac{1}{b\delta}\left(\operatorname{arccoth}\frac{1 - aR_{f,0}}{bR_{f,0}}\right)$$

$$K = (a-1)S$$

$$a = \frac{1}{2}\left[R_{f,1} + \frac{R_{f,0} - R_{f,1} + R_{g,1}}{R_{f,0}R_{g,1}}\right]$$

$$R_{f,0} = \frac{R_{f,1}R_{g,2} - R_{f,2}R_{g,1}}{R_{g,2} + R_{g,1}(R_{f,1}R_{g,2} - R_{f,2}R_{g,2} - 1)}$$

$$R_{f,0} = \frac{1 + R_{f,1}R_{g,1} - \sqrt{(1 - R_{f,1}R_{g,1})^2 + 4(R_{g,1}\tau)^2}}{2R_{g,1}}$$

...but we're not done yet!

Interface Reflections Change Film Reflectance, Transmittance

- Real refractive index *n*
  - speed of light in vacuum / speed of light in medium
  - About 1 for air, 1.5 for polymer (paint medium)
- Change in *n* at boundary → "interface" reflection
- Example: interface reflectance at air/polymer boundary
  - Small for collimated light (0.04)
  - Small for diffuse light passing to higher *n* (0.09)
  - LARGE for diffuse light passing to lower *n* (0.60!)
    - Rays striking at angles greater than critical angle $\theta_c = \sin^{-1}(n_{low}/n_{high})$ are totally internally reflected
- **Film reflectance, transmittance observed in spectrometer depend on interface reflectances**

1st Model Improvement:
Correcting Film Reflectance & Transmittance

- Need corrected reflectance, transmittance (absent interface effects) as inputs to K-M model
- Standard adjustment (Saunderson) corrects only film reflectance
  - Permits calculation of *K*, *S* from film reflectances measured over two different opaque backgrounds (e.g., black, white)
- **Our new approach corrects both film reflectance <u>and film transmittance</u>**
  - Permits calculation of *K*, *S* from reflectance and transmittance of single free film (more accurate)
- Still need to determine magnitudes of interface reflectances (a second issue)

Our 1st Extension of K-M Model
(Correcting Film Reflectance, Transmittance)

- Following terms used in K-M solution (film properties $\rightarrow$ pigment properties)

$$R_{f,0} = \frac{A - B\sqrt{C}}{D}$$

$$\begin{aligned}
A &= \left(1 - R^i_\alpha\right)^2 \left(1 - R^i_\gamma\right)^2 \left(1 + R_{f,1}R_{g,1}\right) R_{g,1} \\
&\quad +2\left(R_{g,1} - R^j_\alpha R^i_\gamma R_{f,1}\right)\left(\left[\left(1 + R_{f,1}R_{g,1}\right) R^i_\gamma - R_{g,1}\right] R^j_\alpha - R^i_\gamma R_{g,1}\right)\tilde{T}^2 \\
B &= \left(1 - R^i_\alpha\right)\left(1 - R^i_\gamma\right) R_{g,1} \\
C &= \left(1 - R^i_\alpha\right)^2 \left(1 - R^i_\gamma\right)^2 \left(1 + R_{f,1}R_{g,1}\right)^2 \\
&\quad +4\left(1 - R^j_\alpha R_{f,1}\right)\left(1 - R^i_\gamma R_{f,1}\right)\left(R^j_\alpha - R_{g,1}\right)\left(R^i_\gamma - R_{g,1}\right)\tilde{T}^2 \\
D &= 2\left[\left(1 - R^i_\alpha\right)^2 \left(1 - R^i_\gamma\right)^2 R^2_{g,1} - \left(R^i_\gamma R_{g,1} - R^j_\alpha\left[\left(1 + R_{f,1}R_{g,1}\right) R^i_\gamma - R_{g,1}\right]\right)\tilde{T}^2\right]
\end{aligned}$$

$$\tau = \frac{-(1 - R^i_\alpha)(1 - R^i_\gamma) + \sqrt{\left[(1 - R^i_\alpha)(1 - R^i_\gamma)\right]^2 + 4R^j_\alpha R^i_\gamma(1 - R_{f,0}R^i_\gamma)(1 - R^j_\alpha R_{f,0})\tilde{T}^2}}{2R^j_\alpha R^i_\gamma \tilde{T}}$$

2^{nd} Model Improvement: Computing Interface Reflectances

- Light incompletely diffuse in weakly scattering pigmented films
  - Incident sunlight ~20% diffuse
  - Incident spectrometer beam 0% diffuse
  - Weakly scattering films slowly diffuse collimated light
- Interface reflectance depends on diffuse fraction (ratio of diffuse flux to total flux)
- **We extend K-M model to better estimate diffuse fractions and interface reflectances at film boundaries**

Our 2nd Extension of K-M Model
(Algorithm to Compute Interface Reflectances)

- Iterative solution couples diffuse fraction q and interface reflectance ω at each boundary to K, S

$$q_0^i = 1 - i_c(0)/i(0)$$

$$q_\delta^j = 1 - j_c(\delta)/j(\delta)$$

$$i(0) = \tilde{T}/(1 - \omega_0^i)$$

$$j(\delta) = (\tilde{R}_f - \omega_\delta^i)/(1 - \omega_\delta^j)$$

$$i_c(0) = \tilde{T}_c/(1 - \omega_{c,0}^i) = \frac{(1 - \omega_{c,\delta}^i)\tau_c}{1 - \tau_c^2 \omega_{c,\delta}^j \omega_{c,0}^i}$$

$$j_c(\delta) = (\tilde{R}_c - \omega_{c,\delta}^i)/(1 - \omega_{c,\delta}^j) = \frac{(1 - \omega_{c,\delta}^i)\omega_{c,0}^i \tau_c^2}{1 - \tau_c^2 \omega_{c,\delta}^j \omega_{c,0}^i}$$

$$\tau_c = \exp\left\{-[K + (1-\sigma)^{-1} S]\delta/\eta\right\}$$

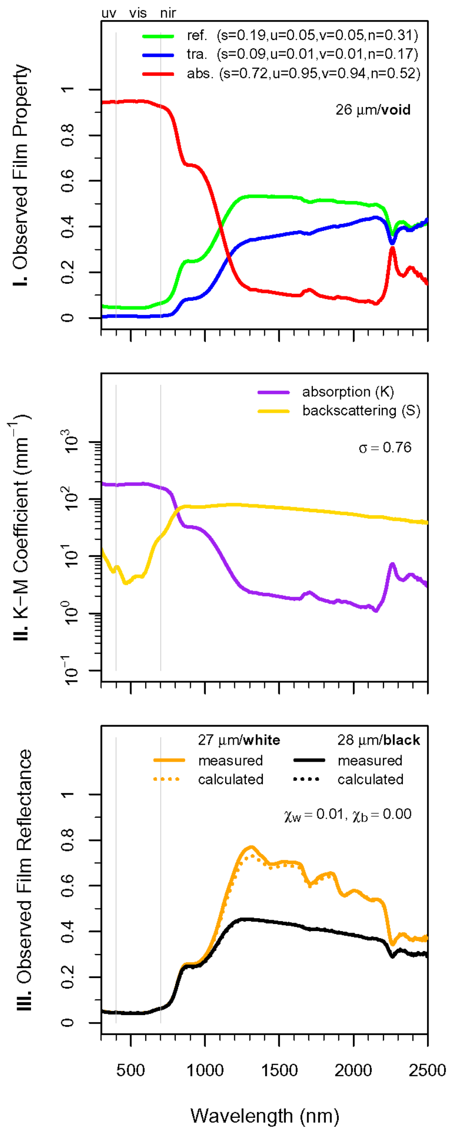
Summary of Our Improvements to Two-Flux K-M Model

- Kubelka-Munk theory extended to
  - Correct both film reflectance and transmittance for effects of interface reflectances
  - Estimate magnitudes of interface reflectances
- Retain compact radiative description of pigment using only two spectral parameters (*K*, *S*)
- Iteratively solve for absorption, scattering, diffuse fractions, interface reflectances
- About 1,500 lines of code

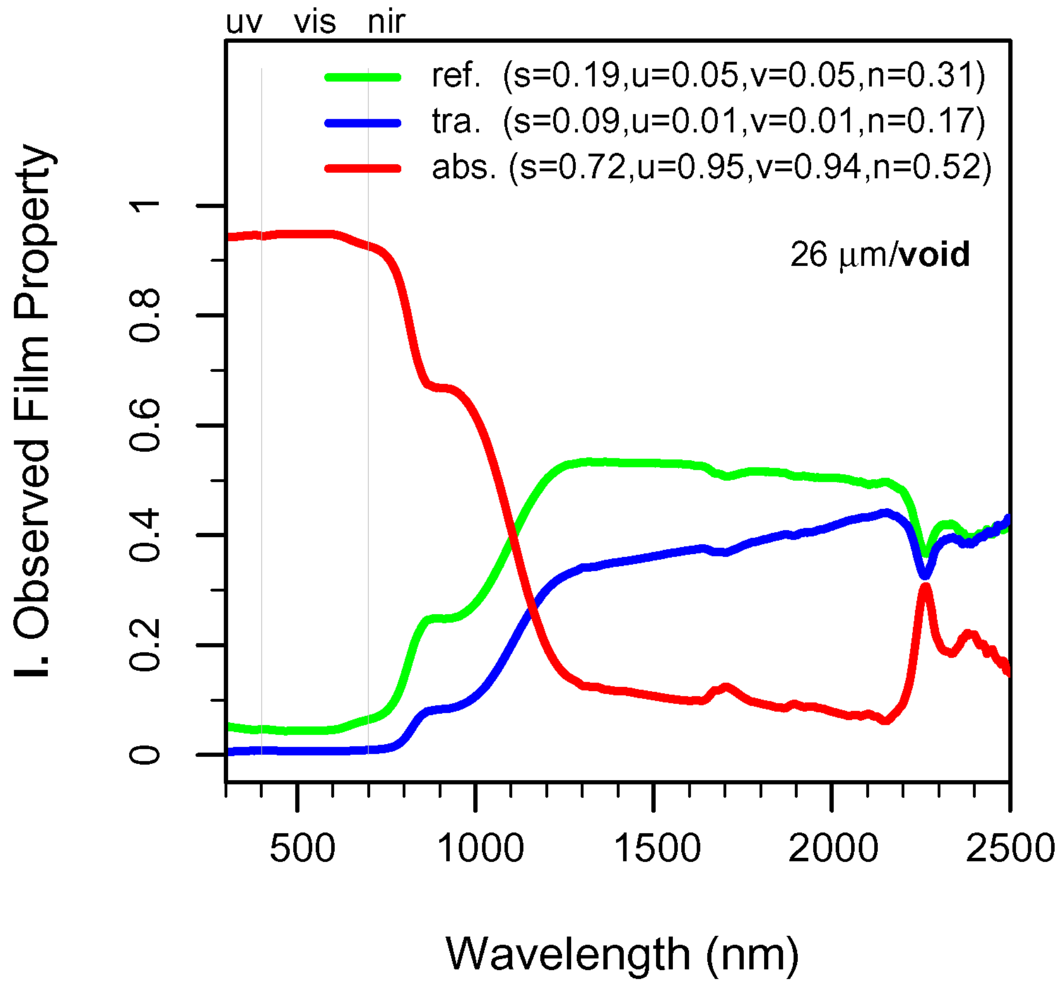
Our Process for Calculating Solar Spectral *K* and *S*

- Three inputs (measurements)
  - Free-film reflectance
  - Free-film transmittance
  - Reflectance of film with opaque black background
- Three outputs (calculations)
  - Absorption coefficient *K*
  - Backscattering coefficient *S*
  - Diffuse fraction *q*
- Validation of results
  - Compare predicted reflectance of film over opaque white background to measured value (not an input to model)

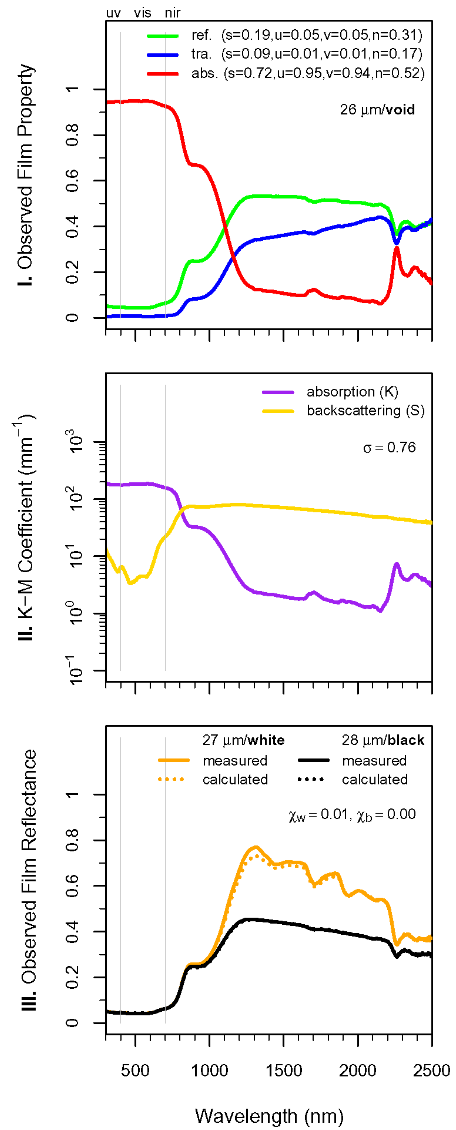
1. Measure Free-Film Reflectance, Transmittance



- **Chromium Green-Black Hematite Modified (Cool Black)**
- **25-μm film with 7% pigment volume concentration**



2. Calculate K-M Coefficients (Absorption *K*, Backscattering *S*)



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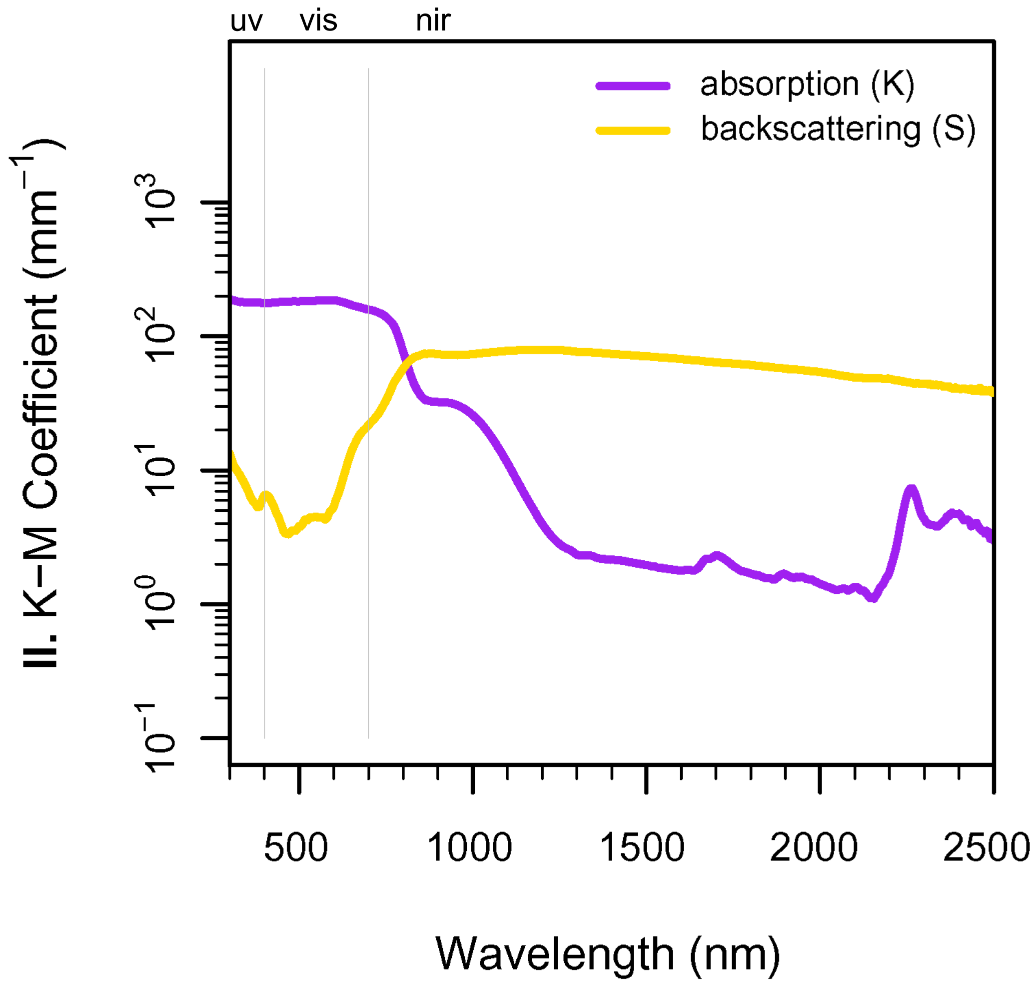
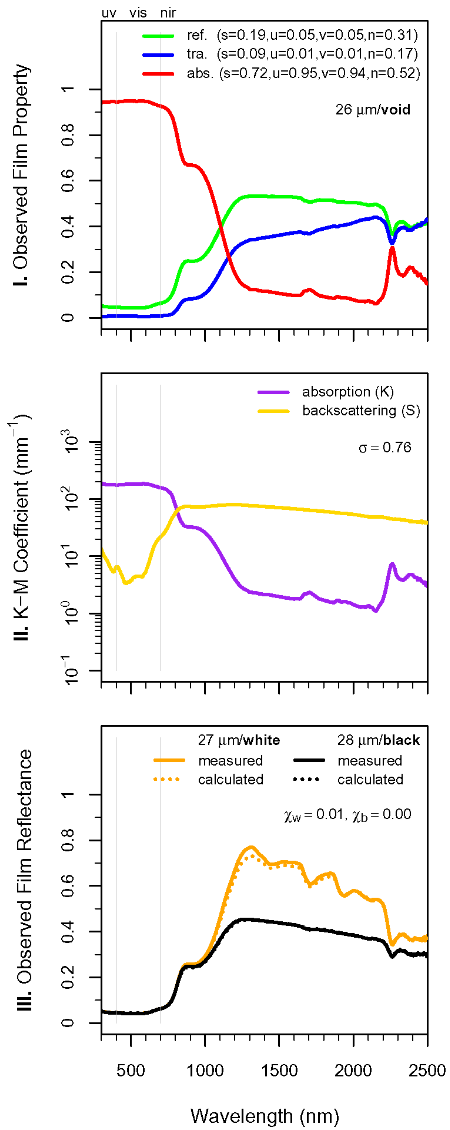


3. Compare Calculated, Measured Reflectances Over White, Black



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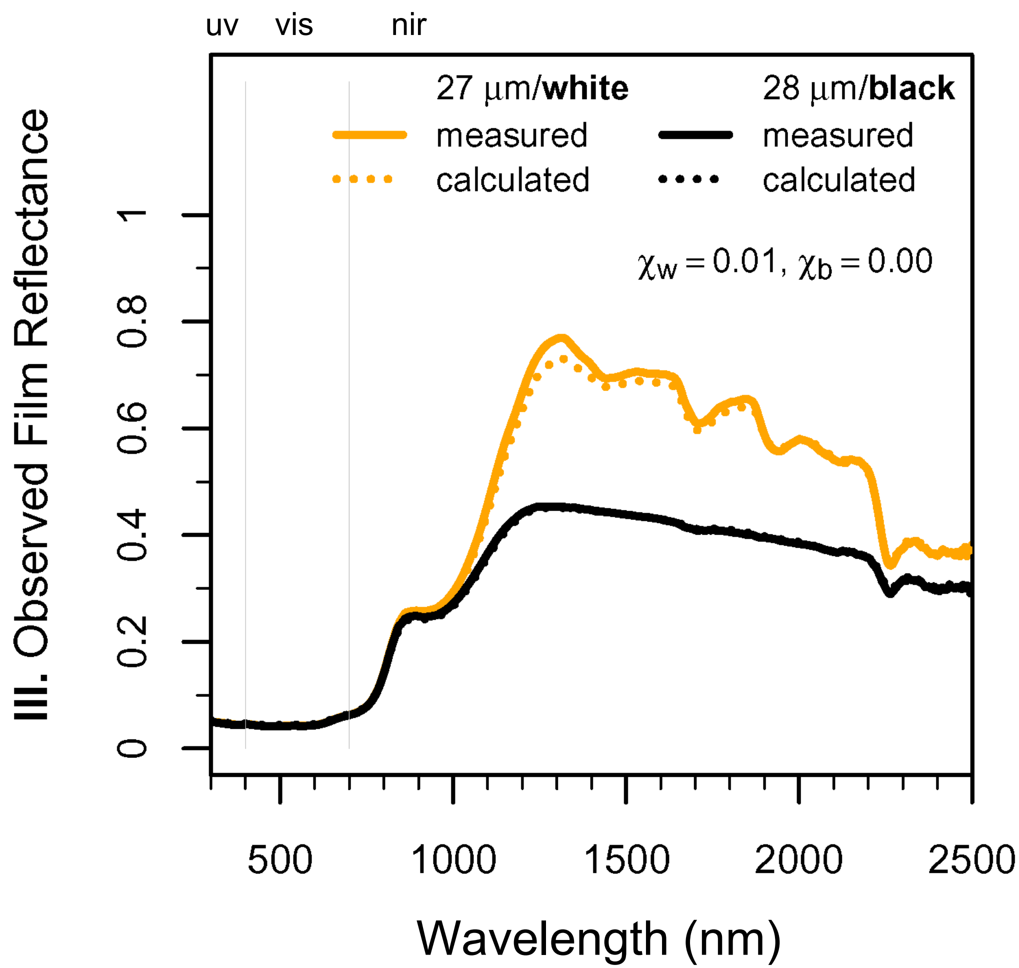
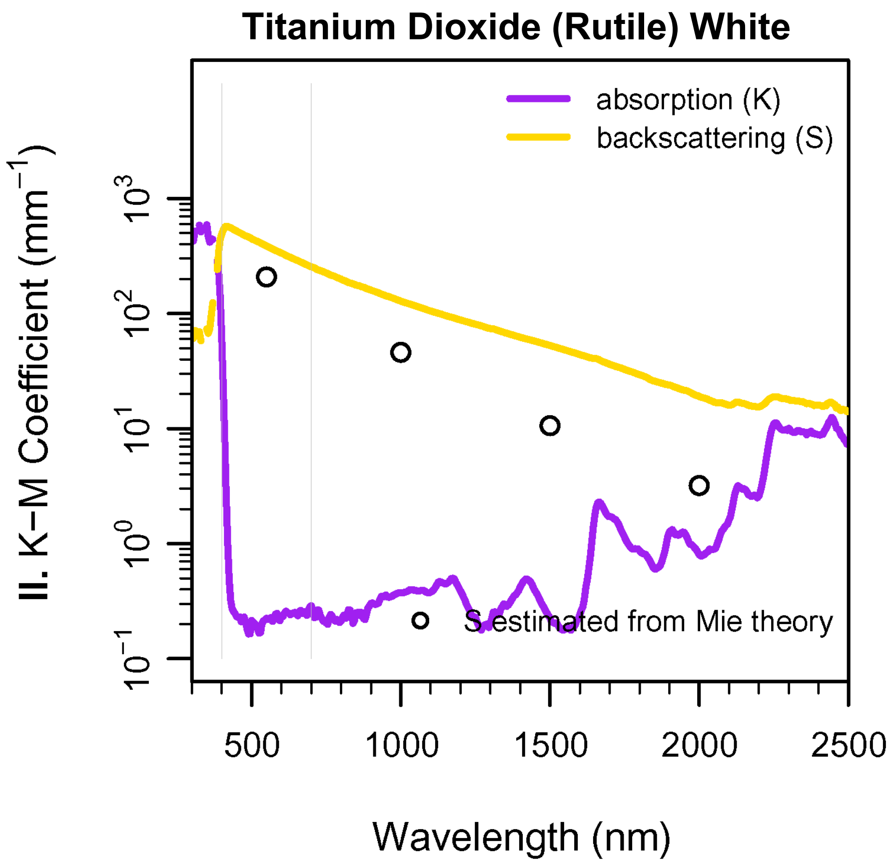


Computing Backscattering *S*: Our Model vs. Mie Theory

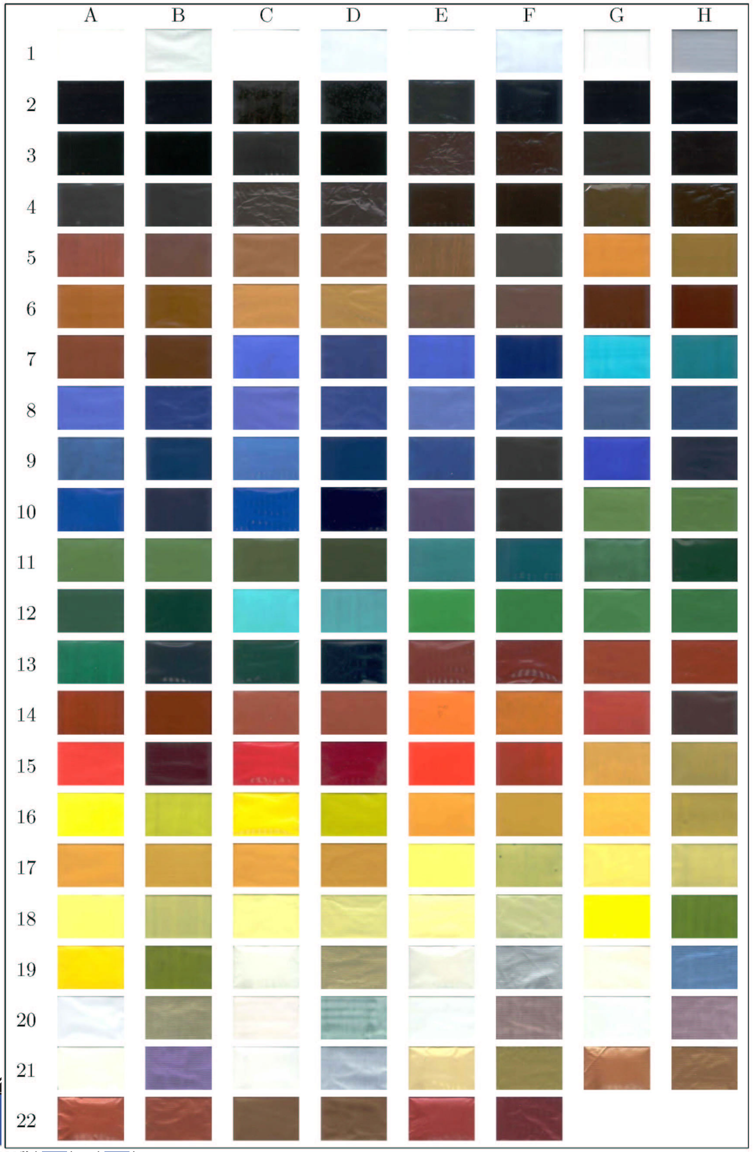
- Upper curve (gold) = our model
- Open circles = Mie theory for scattering by spheres, plus simple multiple scattering theory
  - 200-nm TiO_2 spheres, n=2.7
  - Transparent medium, n=1.5
- Agreement fair in visible range
- Experimental deficit in the NIR believed due to clumping of pigment particles



Part III

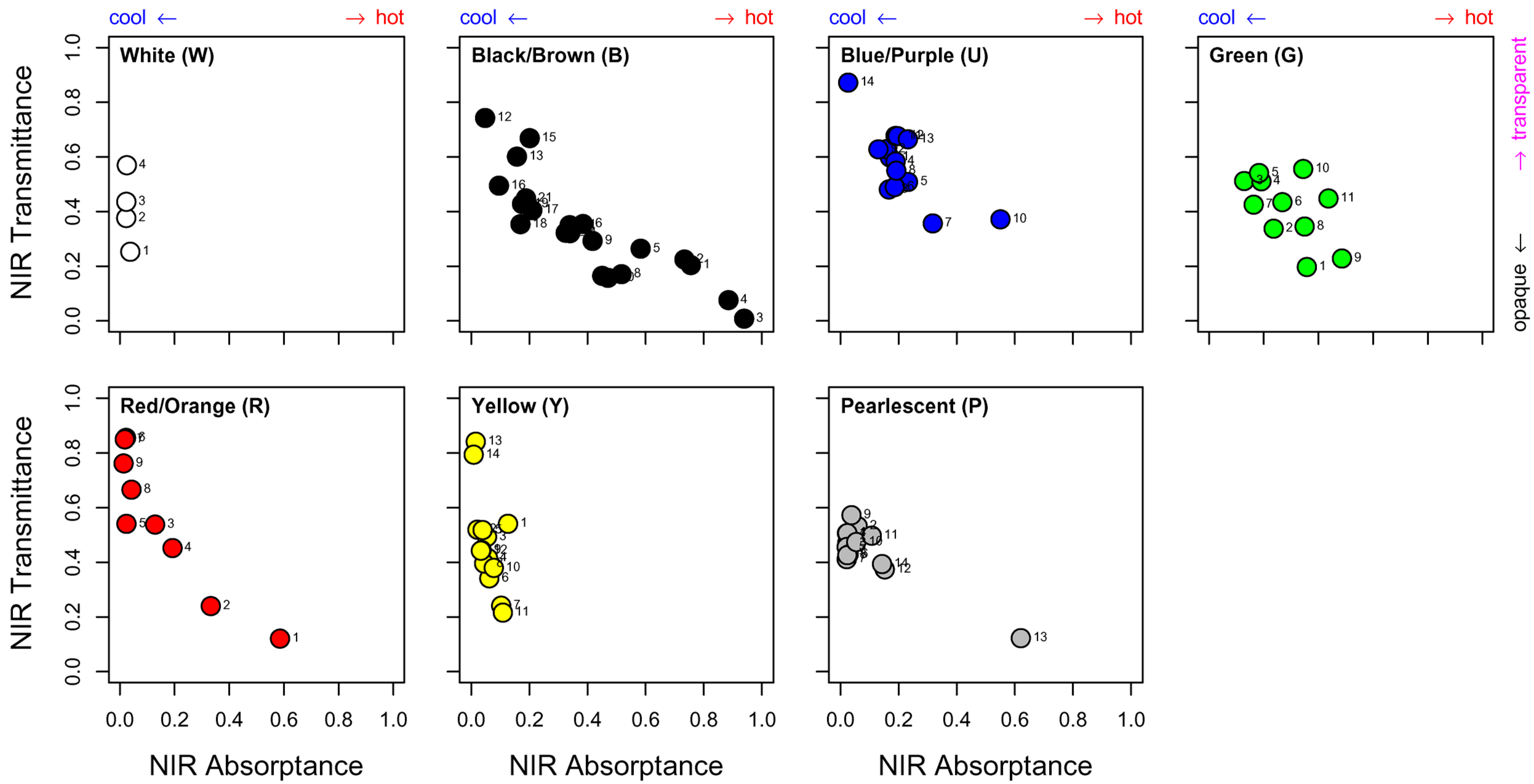
Identifying Cool, Hot Pigments

87 Pigmented Films Characterized



- Single-pigment films (most)
- Each film shown over white, then over black
- Palette
  - 4 white
  - 21 black/brown
  - 14 blue/purple
  - 11 green
  - 9 red/orange
  - 14 yellow
  - 14 pearlescent

Visualizing NIR Performance of Pigmented Films



- Cool, NIR-scattering pigments (*lower left*) suitable for any background
- Cool, NIR-transmitting pigments (*upper left*) need cool background
- Hot pigments (*right side*) to be avoided in cool coatings

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Examples of Cool Pigments

- **All are weak NIR absorbers**
- <u>Strong NIR scatterers</u> (suitable for any substrate)
  - TiO_2 white
  - Nickel titanate and chrome titanate yellows
  - Mixed-metal oxide blacks – $(Fe,Cr)_2O_3$, many related compounds
  - Co_2TiO_4 teal (bluish green)
  - TiO_2 on mica flakes - various colors
- <u>Weak NIR scatterers</u> (need NIR-reflective substrate)
  - Cobalt chromite, cobalt aluminate, and ultramarine blues
  - Some iron oxide browns (burnt sienna, raw sienna)
  - Many organics (perylene black, phthalo blue, quinacridone red...)

Examples of Hot Pigments

- **All are strong NIR absorbers**
- Carbon black (also lamp black, ivory black)
- Fe_3O_4 black (magnetite)
- Copper chromite black
- Iron blue $KFe_2(CN)_6{\cdot}H_20$

Two Articles for *Journal of Applied Physics*

- To be submitted pending internal review
- *Radiative Model*
  - Levinson, R., P. Berdahl, and H. Akbari. Spectral solar optical properties of pigments, Part I: Model for deriving scattering and absorption coefficients from transmittance and reflectance measurements
- *Pigment Survey*
  - Levinson, R., P. Berdahl, and H. Akbari. Spectral solar optical properties of pigments, Part II: Survey of common colorants

Pigment Database

- Details 87 pigmented films
- Solar spectral measurements, calculations
- Shared w/industrial partners
- To be used in our cool-color coating design software (under development)

Ongoing Research

- Characterize paint mixtures
  - Tints (color + white)
  - Nonwhite mixtures
  - Goal: develop accurate model that predicts reflectance of mixtures
- Develop cool-colored coating design software
  - Match color
  - Maximize solar reflectance
  - Use paint-mixture theory, pigment database

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For More Information...

- Visit the Cool Colors website

http://CoolColors.LBL.gov

for copies of

- this presentation
- our pigment characterization papers
- related cool-colors research