Cool Colors for Summer

Characterizing the Radiative Properties of Pigments for Cool Roofs

Ronnen Levinson, Ph.D.
Scientist, Heat Island Group

EETD Noon Seminar
Thursday, 22 April 2004

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 ºC
  - May reduce 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: improving solar reflectance**

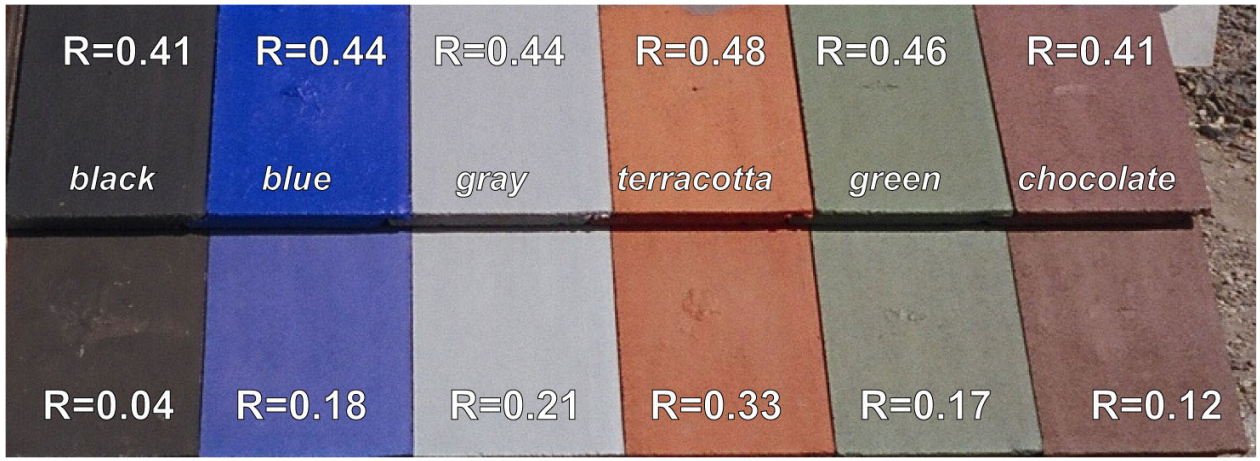
Need for Cool Colors

- 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
  - Use special nonwhite pigments
  - Can match standard colors
  - Can have high solar reflectance, even if dark

Example 1: Cool and Standard Color-Matched Concrete Tiles

Courtesy American Rooftile Coatings



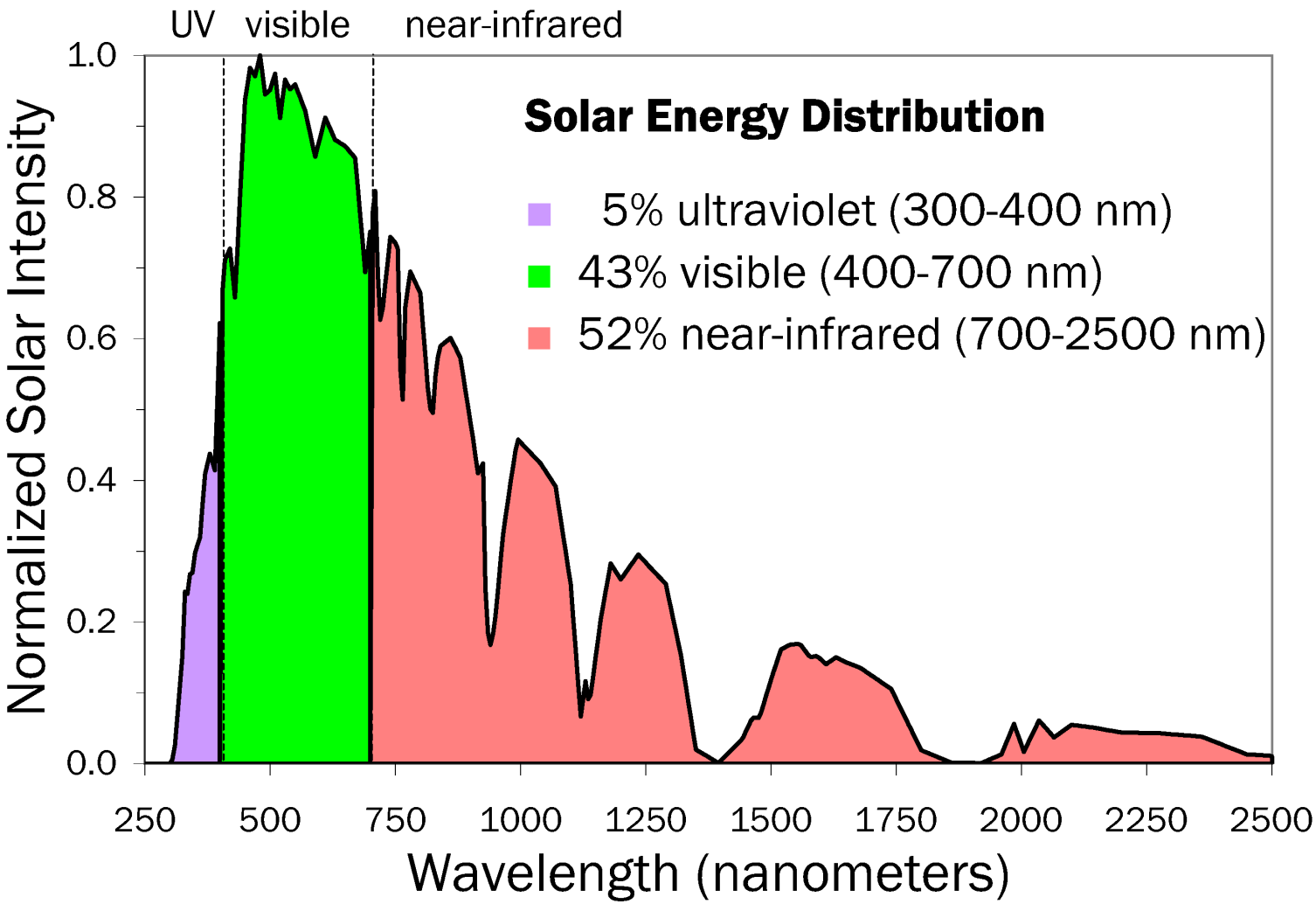
cool

standard

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

- Can increase solar reflectance by up to 0.5
- Gain greatest for dark colors

Cool Colors Reflect Invisible Near-Infrared Sunlight

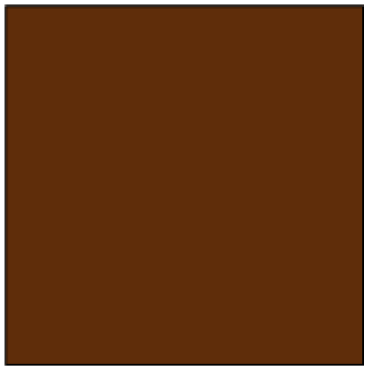


Example 2: Cool and Standard Brown Metal Roofing Panels

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

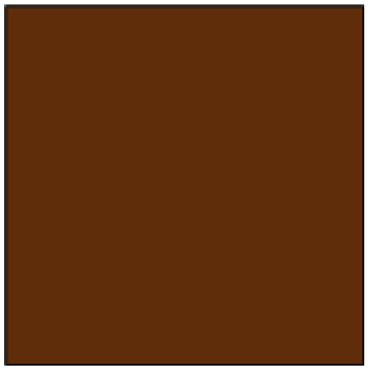
Courtesy BASF Coatings

cool

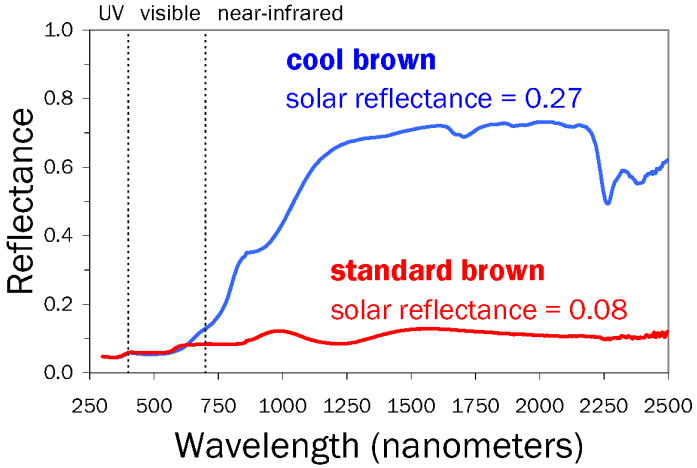


solar reflectance = 0.27
thermal emittance = 0.85
roof temp – air temp = 36ºC (65ºF)

standard



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

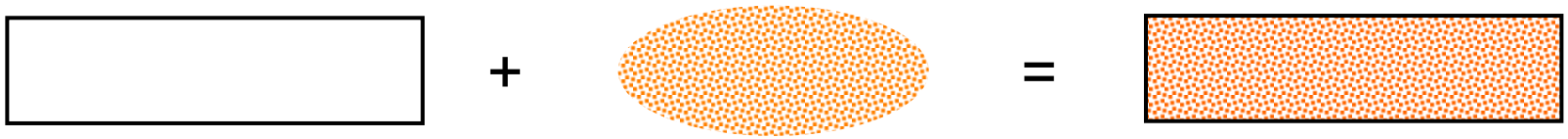


Part II

Characterizing the Solar Spectral Radiative Properties of Pigments

Our Cool Pigment Research

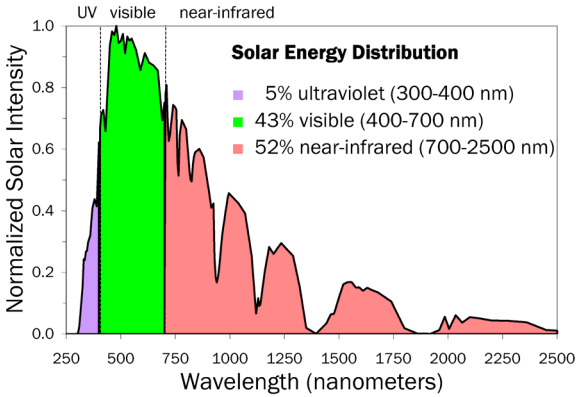
- Objective
  - Improve solar reflectance of architectural coatings by identifying cool and hot pigments
- Approach: investigate **solar spectral** properties
  - Reflectance, transmittance, absorptance of paint films
  - Scattering, absorption by pigments in transparent media



transparent medium | pigment particles | pigmented coating (paint film)

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

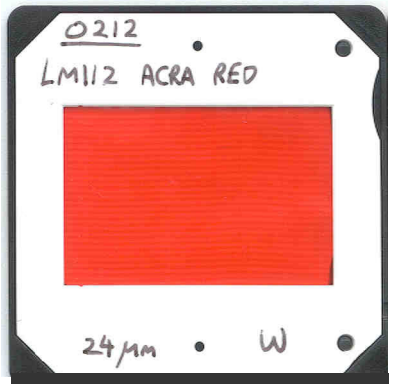
Cool Pigments Scatter and/or Transmit NIR Radiation

- 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

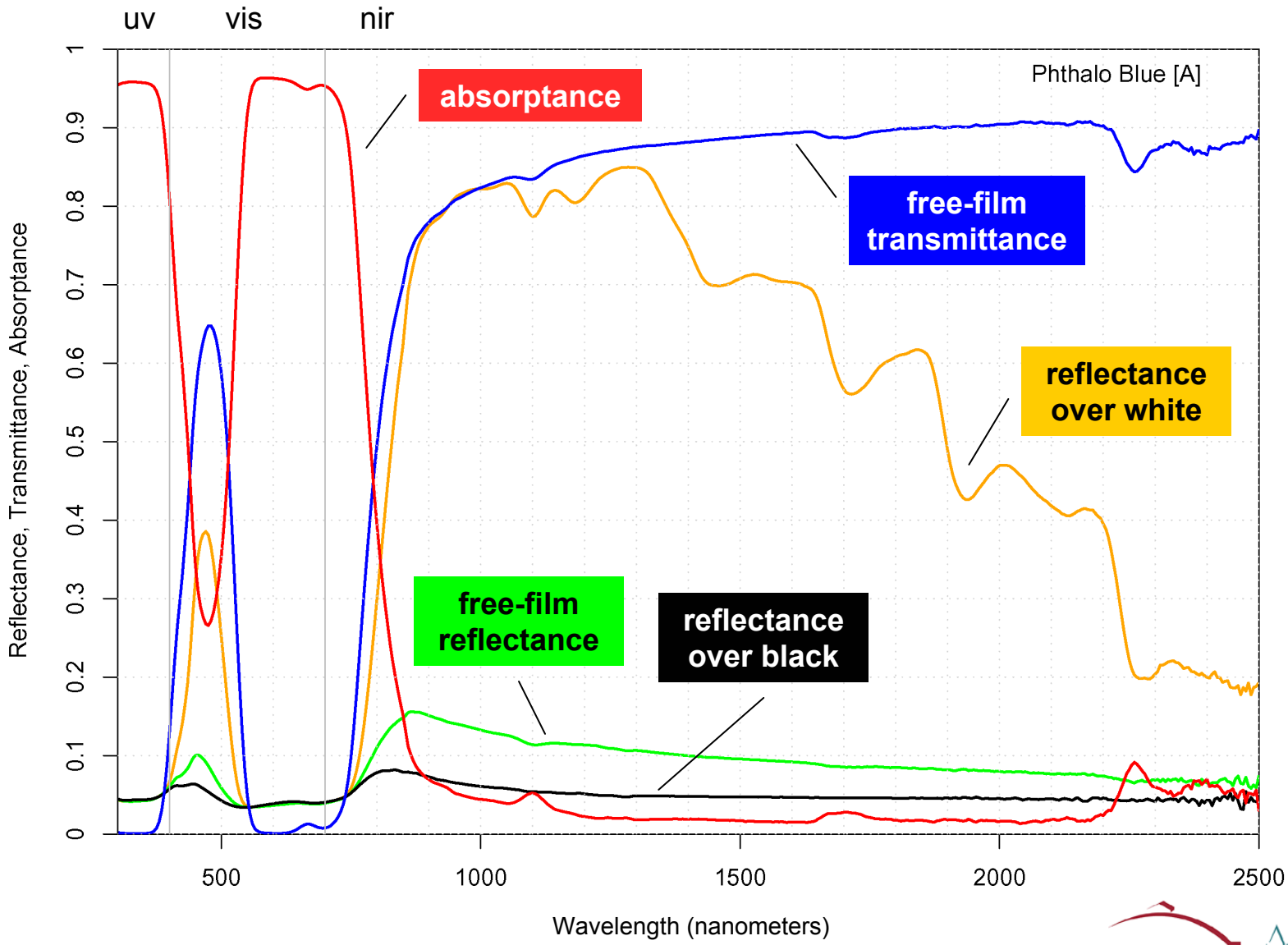
front

back

Measuring Solar Spectral Properties of Pigmented Film

- Four solar spectral measurements
  - Transmittance of free film
  - Reflectance of free film
  - Reflectance of film over opaque white
  - Reflectance of film over opaque black
- Measurements span 300 - 2,500 nm @ 5 nm

Sample Film Measurements



Estimating Absorption, Scattering Via Empirical Continuum Model

- Treat pigmented film as continuum
- Reflectance, transmittance ↔ scattering, absorption
- Simple model (Kubelka-Munk)
  - Assumes perfectly diffuse light
  - Inputs two spectral measurements
    - reflectance and transmittance of free film, or
    - reflectances of film over two different backgrounds
  - Simple solutions
- Complex model (Maheu-Letoulouzan-Gouesbet)
  - Allow partially diffuse light (more realistic)
  - Requires four spectral measurements
  - Solutions available but unwieldy

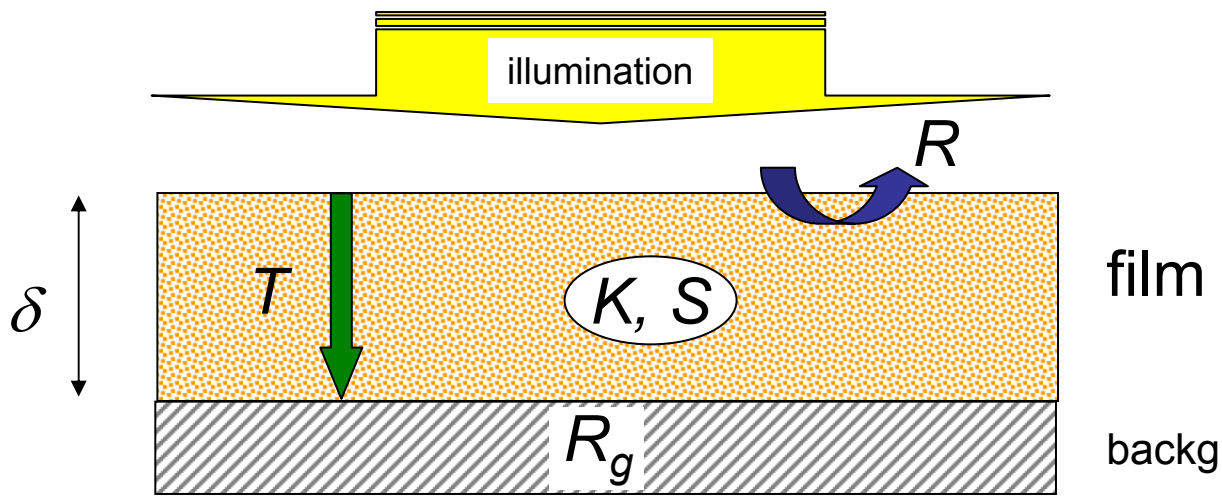
Simplest Continuum Model: Kubelka-Munk (K-M) Two-Flux

Relates pigmented-film properties...

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

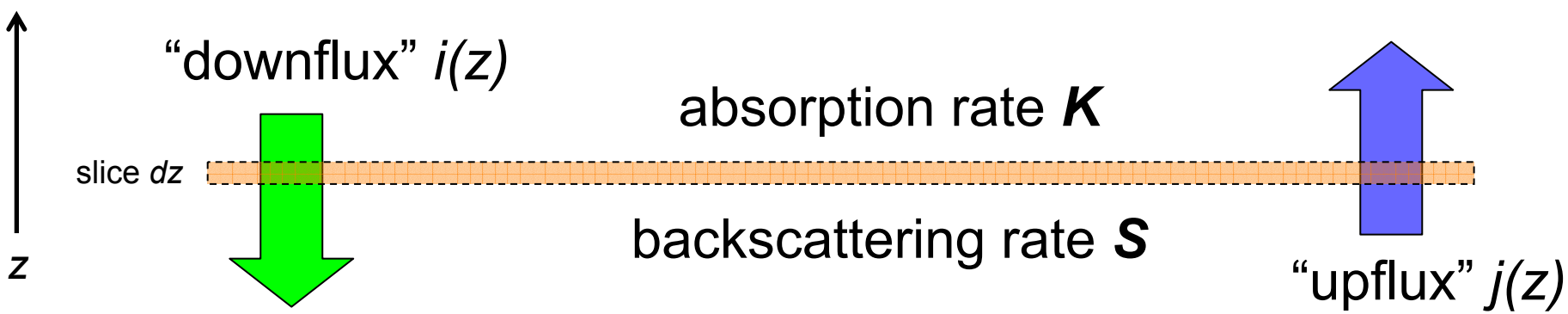
...to properties of pigment (in transparent medium)

- 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

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

- 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 → pigment properties)

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

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

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

2nd 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

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

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

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

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

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

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

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

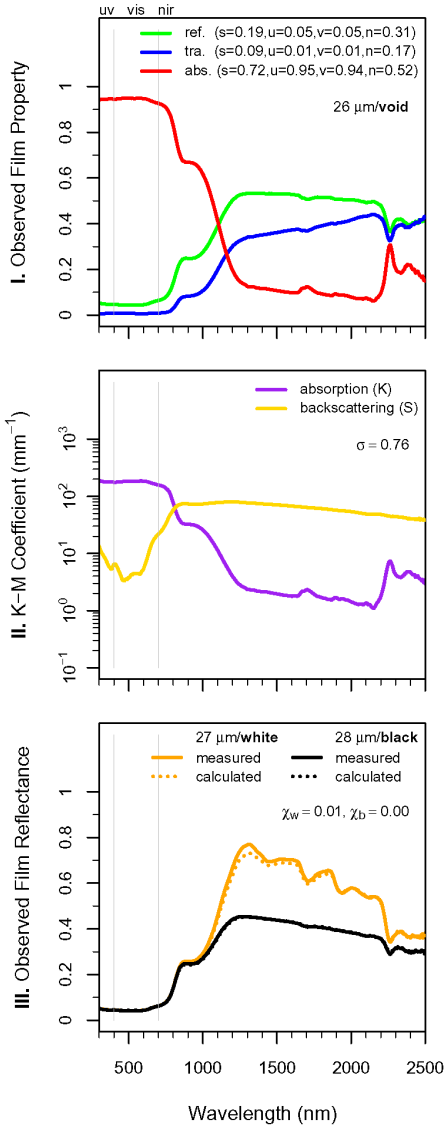
Summary of Our Improvements to Two-Flux K-M Model

- Kubelka-Munk theory extended to
  - Correct both film reflectance <u>and transmittance</u> for effects of interface reflectances
  - Estimate magnitudes of interface reflectances
- Iteratively solve for absorption, scattering, diffuse fractions, interface reflectances
- About 1,500 lines of code

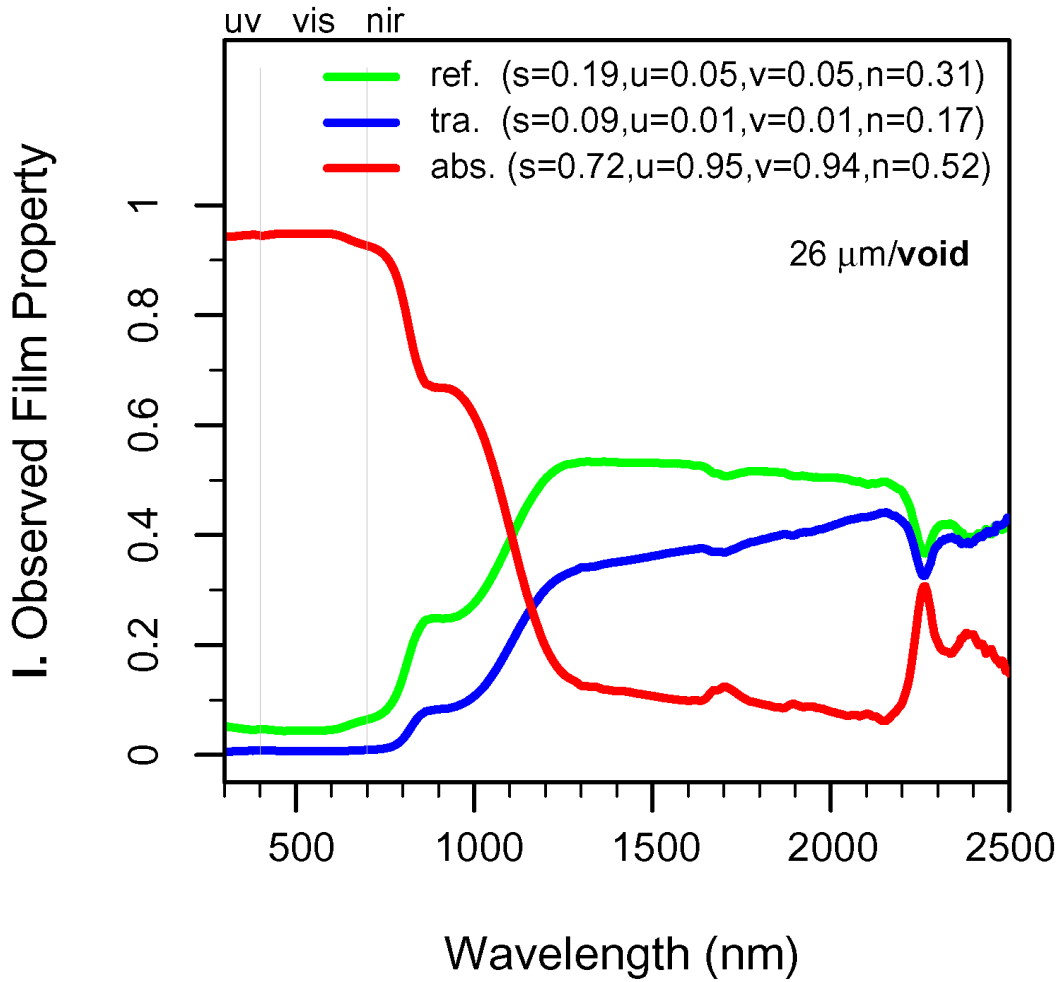
Our Process for Calculating Solar Spectral *K* and *S*

- 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)

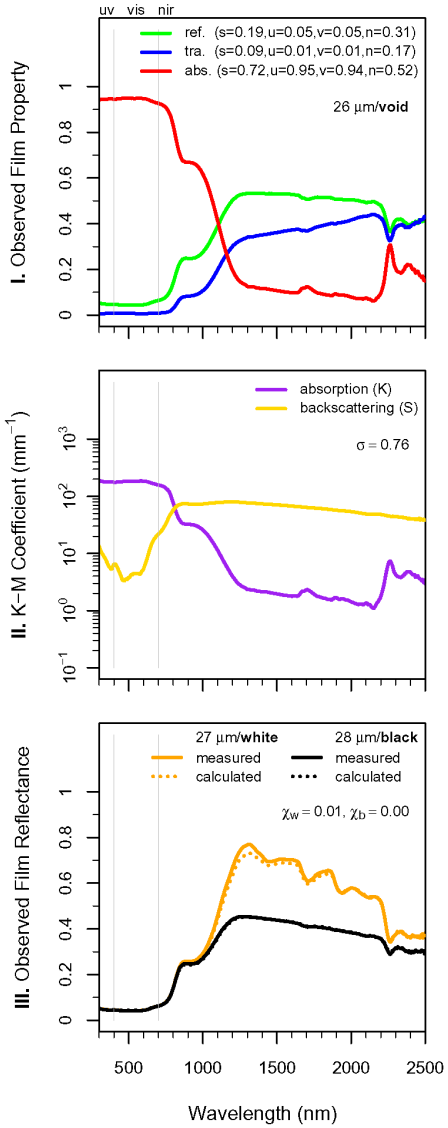
1. Measure Free-Film Reflectance, Transmittance



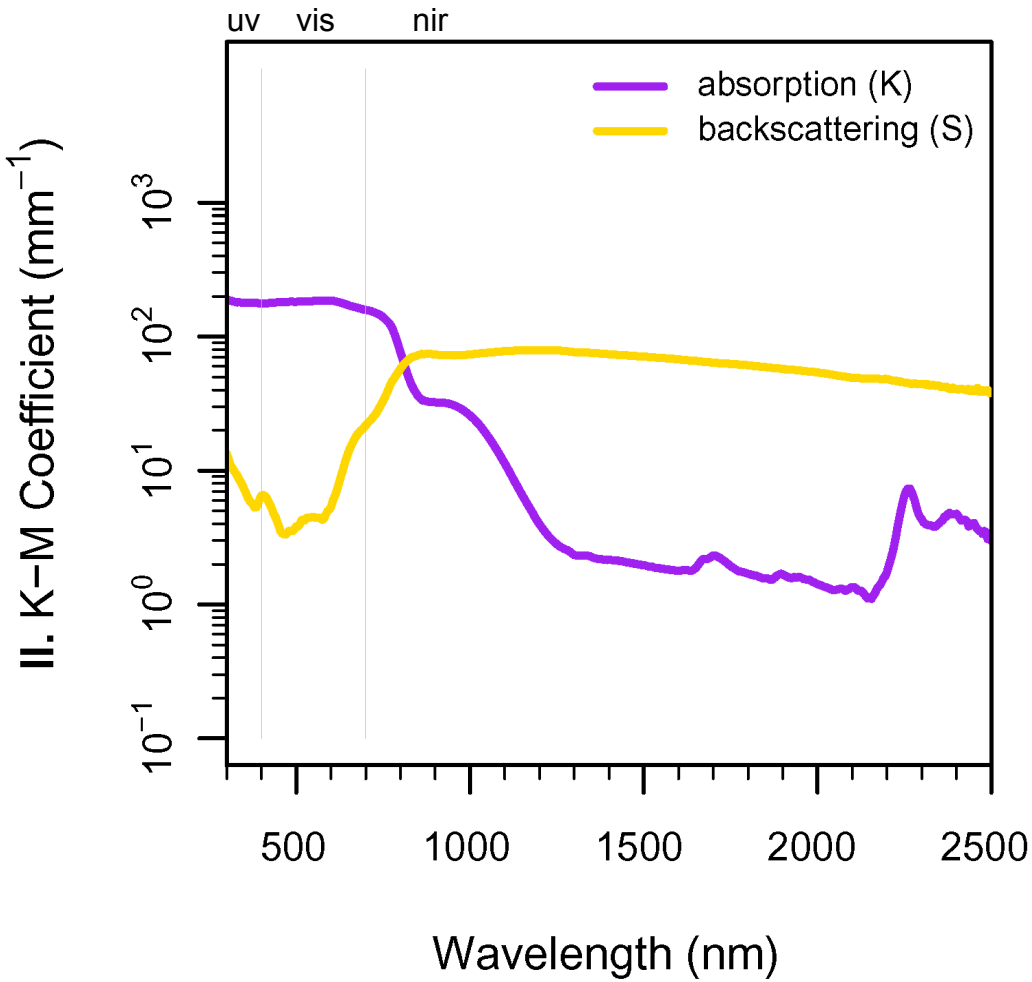
- **Chromium Green-Black Hematite Modified (Cool Black)**
- **25-µm film with 7% pigment volume concentration**



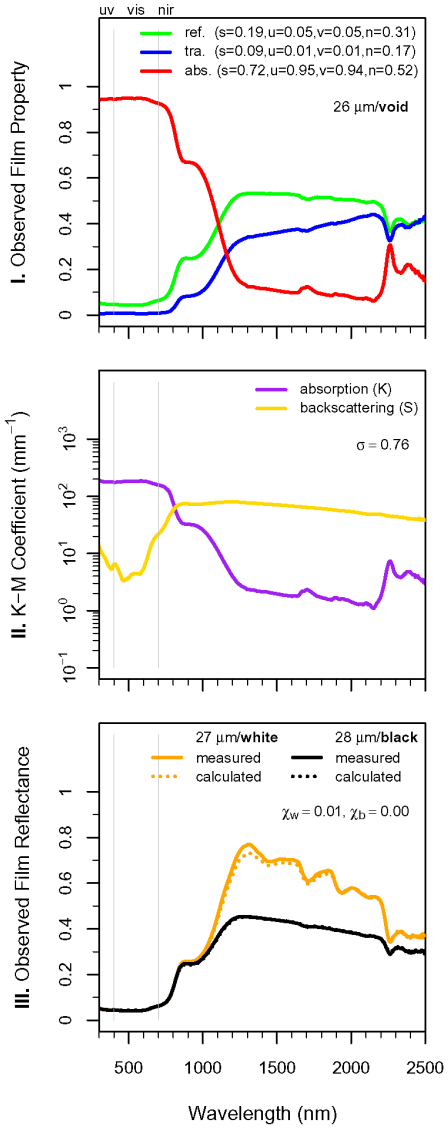
2. Calculate K-M Coefficients (Absorption *K*, Backscattering *S*)



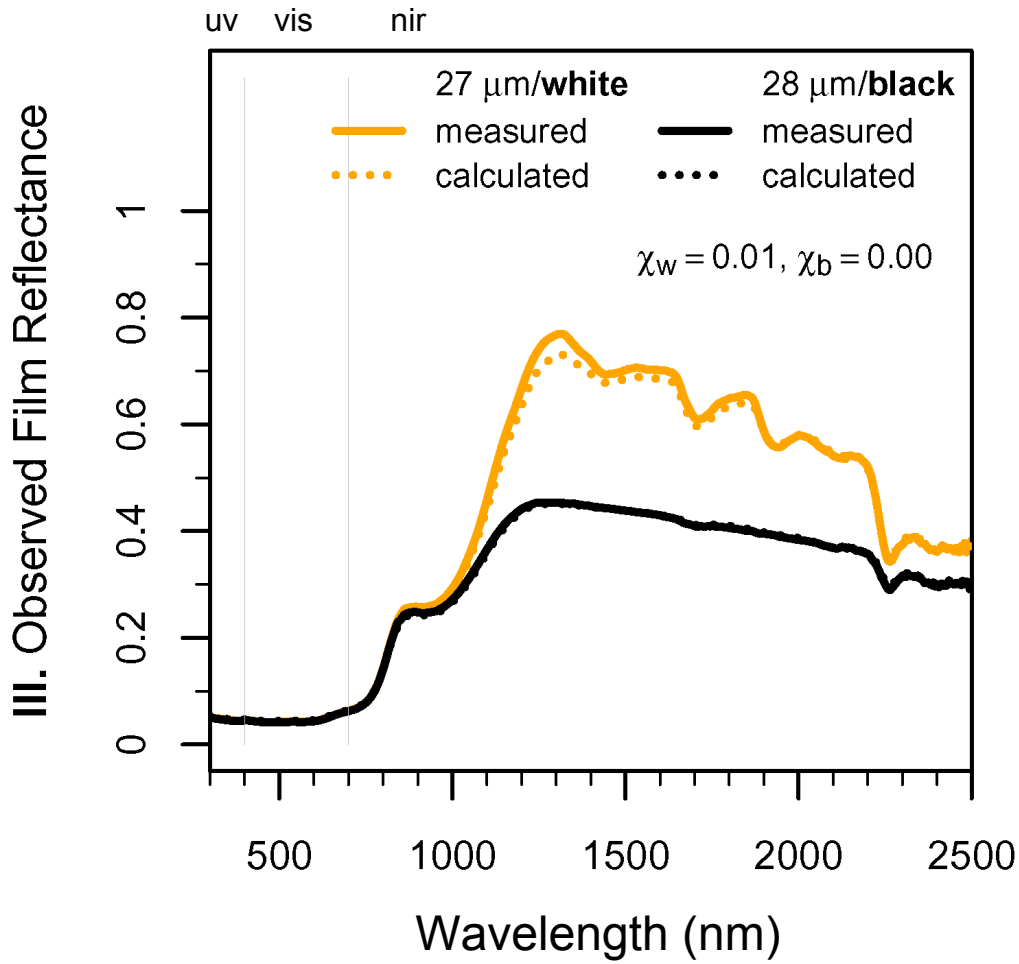
- **Chromium Green-Black Hematite Modified (Cool Black)**
- **25-µm film with 7% pigment volume concentration**



3. Compare Calculated, Measured Reflectances Over White, Black

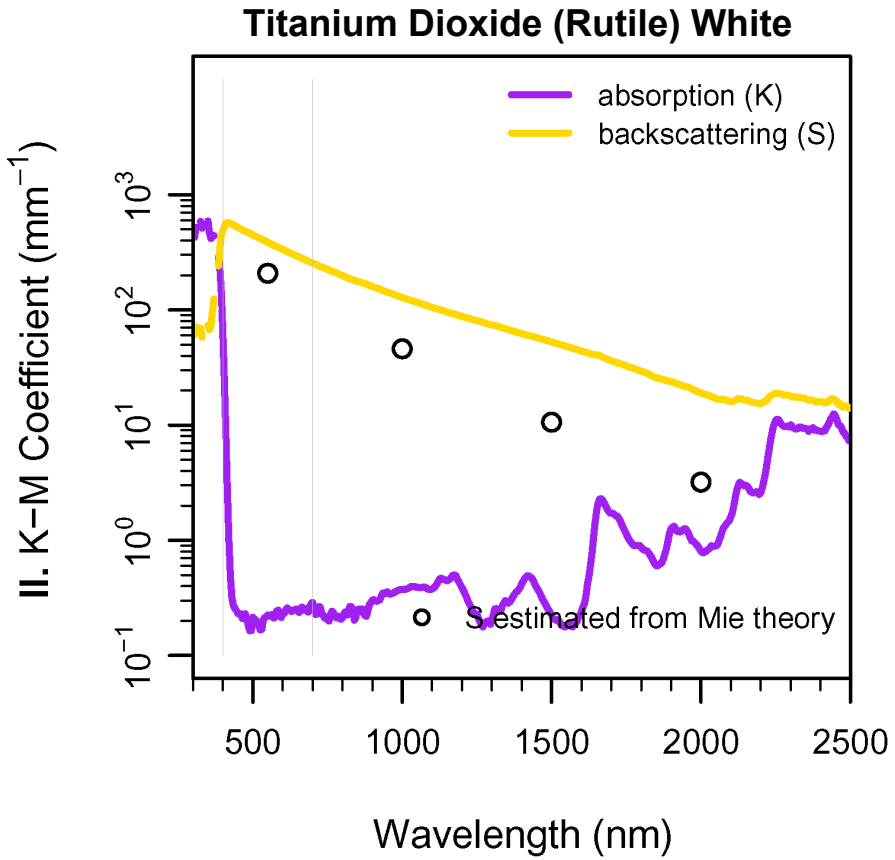


- **Chromium Green-Black Hematite Modified (Cool Black)**
- **25-µm film with 7% pigment volume concentration**



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

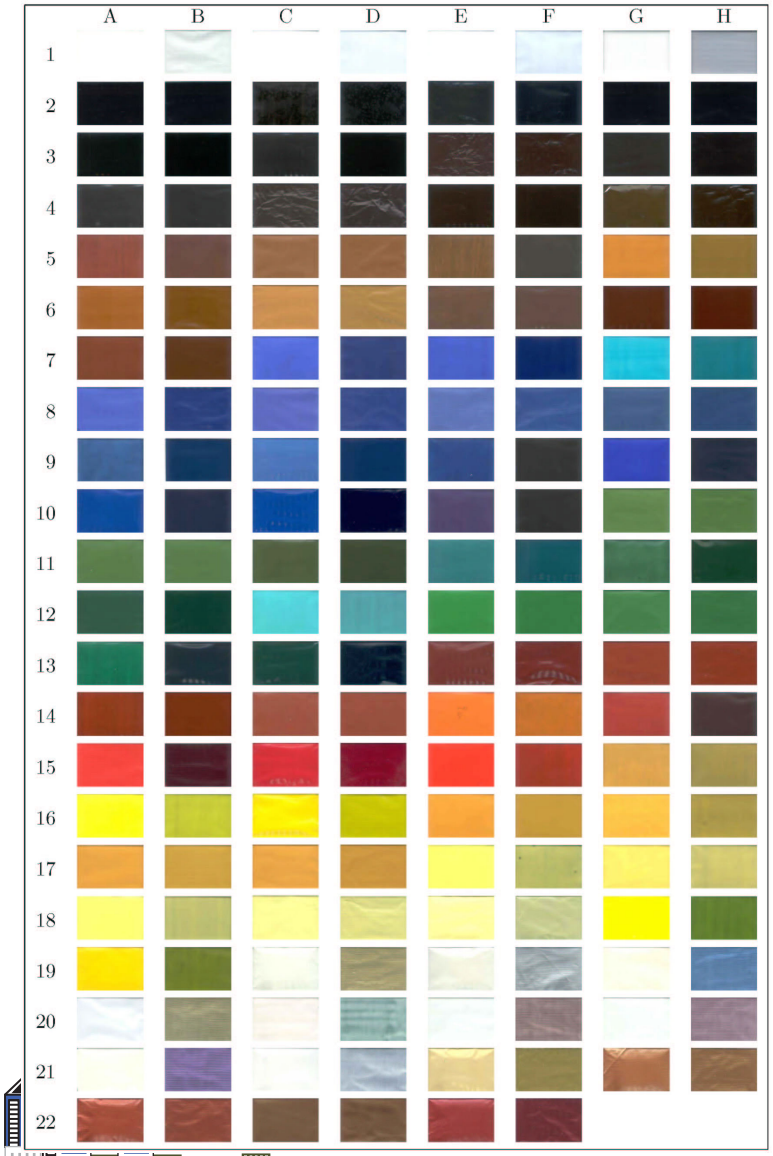
- Upper curve (gold) = our model
- Open circles = Mie theory for scattering by spheres, plus simple multiple scattering theory
  - 200-nm TiO_2 spheres, n=2.7
  - Transparent medium, n=1.5
- Agreement fair in visible range
- Experimental deficit in the NIR believed due to clumping of pigment particles



Part III

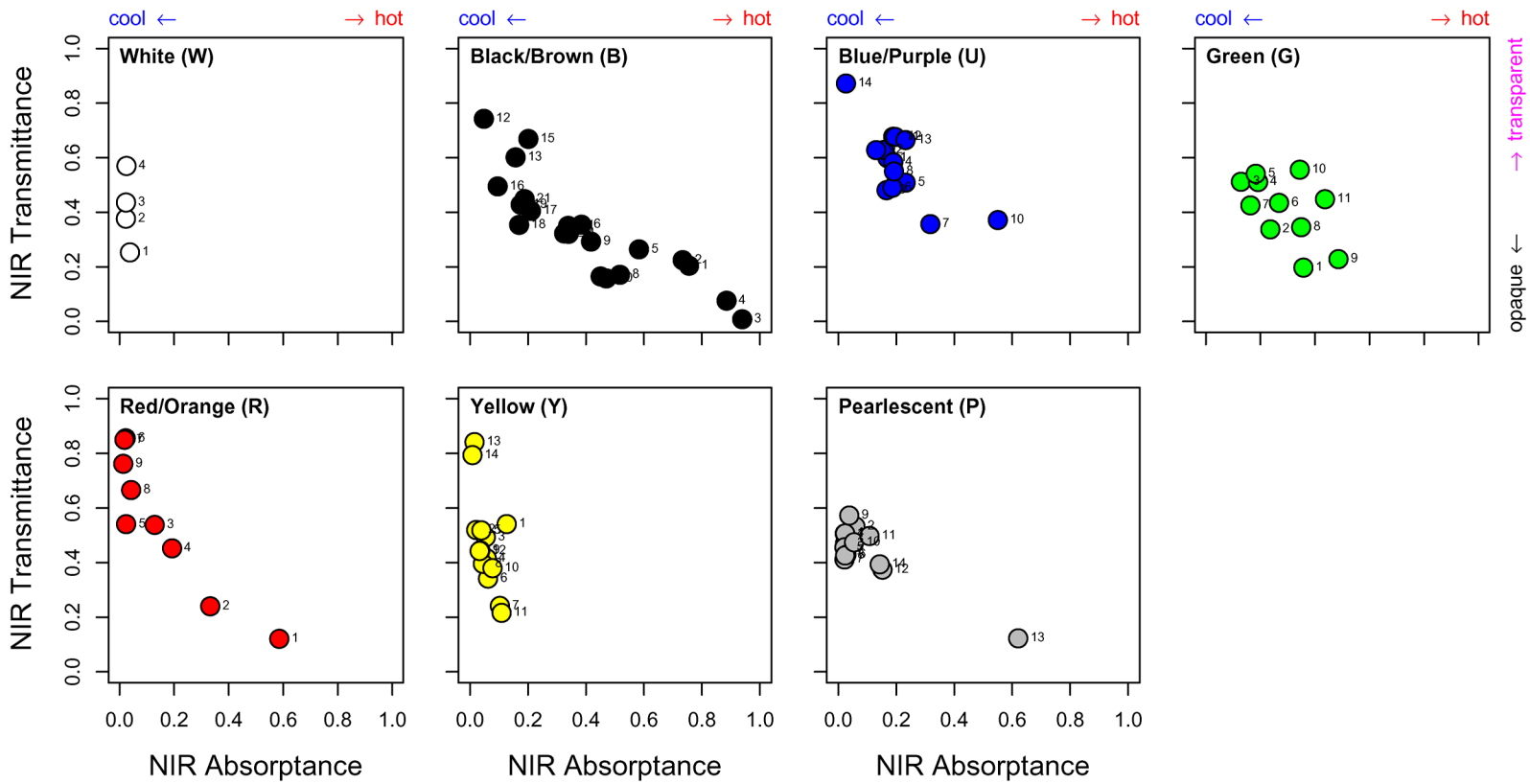
Identifying Cool, Hot Pigments

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

Examples of Cool Pigments

- **All are weak NIR absorbers**
- Strong NIR scatterers (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
- Weak NIR scatterers (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

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