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

New

- pitched, cool & colored

- pitched, white
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

**Solar Energy Distribution**

- 5% ultraviolet (300-400 nm)
- 43% visible (400-700 nm)
- 52% near-infrared (700-2500 nm)
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

- Solar reflectance gains typically about 0.3
- Gains greatest for dark colors
Example 2: Cool and Standard Brown Metal Roofing Panels

- Solar reflectance ~ 0.2 higher
- Afternoon surface temperature ~ 10°C lower

Courtesy BASF Coatings

![Cool and Standard Brown Metal Roofing Panels](image)
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

\[
\text{transparent medium} + \text{pigment particles} = \text{pigmented coating (paint film)}
\]
Near-Infrared Absorption

- Near-infrared (NIR) radiation
  - Invisible
  - 0.7 - 2.5 \( \mu \text{m} \)
  - 52% of sunlight

- Absorption converts light to heat
  - Strong NIR absorption \( \rightarrow \) hot pigment
  - Weak NIR absorption \( \rightarrow \) 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

acra red over opaque black
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
Sample Film Measurements

Reflectance over white

Free-film transmittance

Absorptance

Reflectance over black

Wavelength (nanometers)
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 ($\delta$), 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
  \[-\frac{di}{dz} = -(K + S) i + S j\]  downflux rate of change
  \[\frac{dj}{dz} = -(K + S) j + S i\]  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 \(\{R, T, R_g, \delta\}\) ↔ pigment properties \(\{K, S\}\)
K-M Solutions Are Simple...

Pigment props $\rightarrow$ film props

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

\[ a \equiv \frac{(S + K)}{S} \]
\[ b \equiv \left( a^2 - 1 \right)^{\frac{1}{2}} \]

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

Film props $\rightarrow$ pigment props

\[ S = \frac{1}{b\delta} \left( \text{arccoth} \frac{1-aR_{f,0}}{bR_{f,0}} \right) \]
\[ K = (a - 1)S \]

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

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

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

...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 $\rightarrow$ “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
      $\theta_c=\sin^{-1}(n_{\text{low}}/n_{\text{high}})$ 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 and film transmittance**
  - 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)

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

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

\[
\tau = \frac{-(1 - R_\alpha^i)(1 - R_\gamma^i) + \sqrt{[(1 - R_\alpha^i)(1 - R_\gamma^i)]^2 + 4R_\alpha^i R_\gamma^i(1 - R_{f,0} R_\gamma^i)(1 - R_\alpha^i R_{f,0})\tilde{T}^2}}{2R_\alpha^i R_\gamma^i \tilde{T}}
\]
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 2\textsuperscript{nd} Extension of K-M Model
(Algorithm to Compute Interface Reflectances)

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

\begin{align*}
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^i, 0) = \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\}
\end{align*}
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 $S$)

- Chromium Green-Black Hematite Modified (Cool Black)
- 25-$\mu$m 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

![Graphs showing reflectance measurements and calculations across different wavelengths.](image)
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)$_2$O$_3$, many related compounds
  - Co$_2$TiO$_4$ 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)
- Fe₃O₄ black (magnetite)
- Copper chromite black
- Iron blue KFe₂(CN)₆·H₂O
Two Articles for *Journal of Applied Physics*

- To be submitted pending internal review
- **Radiative Model**
- **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