# Characterization of Absorptivities To Solar Radiation for Colored Pigments in Coatings

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*Colored pigments absorptivities to solar radiation have been characterized quantitatively by measuring the absorption coefficients of the colored pigments mixed in white titanium dioxide standard coating. The standard coating contains white $TiO_2$ with 17% pigment volume concentration (PVC). Dry white coating with more than 134 µm thickness is opaque and used as a dispersion medium for colored pigments. The reflectances of the coatings of white $TiO_2$ and three kinds of colored pigments (perylene black, toluidine red, and benzidine yellow) to solar radiation are measured by means of a UV-3100 recording spectrophotometer operating in the 250~2500 nm spectral range. It is found that the plots of $\lg {}^{1}/_{R}$ (R, reflectance of coating to solar radiation) against ${}^{V_{colored}}/_{V_{TiO_2}}$ (volume ratio of the colored pigment to $TiO_2$ in coating) are straight lines of increasing slopes in the range of ${}^{V_{colored}}/_{V_{TiO_2}}$ less than five percent. From the slopes of the straight lines, the absorption coefficients of colored pigments can be measured quantitatively.*

## INTRODUCTION

Coatings that exhibit complete, selective, or an absence of solar radiation reflectance are required for a wide variety of uses. For architectural applications, coatings can be designed that reflect incident solar radiation and minimize transfer of heat to the interior of the structure, thus reducing the energy required for cooling. Conversely, coatings for solar heat collectors are designed to absorb and retain heat until it can be transferred to a fluid for transport and storage.

For convenience, the spectral energy distribution of solar radiation is usually divided into three bands. The ultraviolet band, between 200 and 400 nm, contains 5% of the energy in sunlight. The energy in the visible band, between 400 and 720 nm, is 45% of all solar energy. The near–infrared band, between 720 and 2500 nm, contains 50% of the energy in sunlight.

Pigments exert the principal influence on the visible and near-infrared properties of coatings. Pigments used in the coatings with tailored solar energy properties are chosen because of their reflectance (including diffuse and specular), absorptance, and transparence in the solar region. For a nontransparent layer, the incident solar radiation can be absorbed and reflected only. The value of the reflection constant changes with the type of pigment, concentration, and particle size. A knowledge of the behavior of pigments in the visible and near-infrared region is a critical factor in formulating coatings to specific requirements.

Many efforts have been undertaken in the study of the characterization of pigment absorptivity. The Kubelka-Munk (KM) theory,[1-4] together with colorimetry, is one of the most important methods in practical pigment testing for visible light region. In fact, it owes its enormous significance to one single equation, for which the name "Kubelka-Munk function" has been adopted. This equation ascribes the reflection of nontransparent layer to the quotient of two material constants which characterize the light absorption and the light reflectance (K/S). The constant K/S is often used as a characterization of absorptivities to visible light for colored pigments in coatings.

By means of a spectrophotometer operating in the visible and near-infrared regions equipped with an integrating sphere, Wake et al.[5] measured the reflectance spectra of dry film containing pigments dispersed in standard resin over the visible and near-infrared range. Measurements of infrared reflectance were made over highly reflecting white ($R_w$) and highly absorbing black ($R_b$) surfaces. They obtained the data for some representative pigments. Using films 75~88 µm in thickness, the contrast ratio ($CR_{IR}$) at 800 nm in the infrared as calculated for each pigment using equation

$$CR_{IR} = \frac{R_b}{R_w} \times 100$$

Wake et al. classified each pigment according to its reflectance and contrast ratio into one of six categories.[5] They found each pigment to be either highly reflective, highly absorbent, transparent, or intermediate in behavior between any two of these categories. When $R_w$ greatly exceeds $R_b$, the pigment is transparent and has little or no hiding power (e.g., amorphous silica, barytes, talc), but similar values of $R_w$ and $R_b$ denote high contrast ratios. Values of $R_w$ and $R_b$ which are similar and high indicate that hiding is principally achieved by diffuse reflectance (such as titanium dioxide), whereas values which are similar and low indicate that hiding is caused by absorption (e.g., dark brown iron oxide, black iron oxide); in both of these cases the contrast ratio is high, usually above 0.90.

Although the characterization method suggested by Wake et al. is used in the visible and near-infrared regions, namely sunlight wavelength range, it is a qualitative one only.

The main purpose of this article is to find an empirical and convenient method that can quantitatively characterize the absorption coefficients to solar radiation for colored pigments in coatings.

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**Table 1—Materials of the Experiments**

| Materials | Specifications | Sources |
|---|---|---|
| HCPE (Higher Chlorinated Polyethylene) | 66% chlorine concentration, Mw=44,968 | Yulong Chemical Technology Co. Fenghua Zhejiang, China |
| $TiO_2$ | $R_{902}$ | Dupont Co. |
| Chlorinated paraffin | 42% chlorine concentration | Guangzhou Agent Co. China |
| Perylene black | — | BASF Co. |
| Toluidine red | DCC 2215 | REHO International Inc. |
| Benzidine yellow | DCC 1202 AAOT | REHO International Inc. |
| Xylene | AR. | Yili Chemical Co. Beijing, China |
| Acetone | AR. | Yili Chemical Co. Beijing, China |

**Table 2—Standard White Coating Formulation**

| Ingredient | Function | Amount (g) | Weight Percent (%) |
|---|---|---|---|
| $TiO_2$ | Pigment | 1.080 | 15.2 |
| HCPE | Resin | 1.650 | 23.3 |
| Chlorinated paraffin | Plasticizer | 0.498 | 7.1 |
| Xylene | Solvent | 3.274 | 46.2 |
| Acetone | Solvent | 0.578 | 8.2 |
| Total | | 7.08 | 100 |
| PVC | 17 % | | |

## EXPERIMENTAL

### Materials and Specimen Preparation

The materials used in this study are shown in *Table* 1. The standard white coating formulation is given in *Table* 2. White standard coatings were prepared as follows:

A mixture of $TiO_2$ and $^1/_3$ amount of HCPE vehicle containing chlorinated paraffin was milled first for five hours. Then, when the rest of the vehicle was added, the system was milled for 19 hr continually before application.

For the preparation of colored coatings based on the same system, a similar paint formulation was used. Again $TiO_2$, colored pigments (perylene black, toluidine red, or benzidine yellow) and HCPE vehicle containing chlorinated paraffin was ground with the same procedure.

The above samples were coated on PET substrate respectively and dried completely in a controlled environment (55% RH and 25°C).

### Measurement of Thickness

The thickness values of white and colored dry coatings were measured by thickness measurer (TDG-1, Guilin Optic Instrument Co. Guangxi, China).

### Measurement of Reflectance

Measurements of reflectance versus a smoked Barium sulfate standard are made using an Φ60 mm integrating sphere of UV-3100 recording spectrophotometer over the range from 250 to 2500 nm. The illumination and viewing mode shall be normal-diffuse. The solar energy reflected is obtained by integrating over a standard solar energy distribution curve using weighted ordinates for the appropriate solar-energy distribution. The distribution at sea level, air mass two, is used.[6]

## RESULTS AND DISCUSSION

### Reflectances of White $TiO_2$ Coatings with Different Thickness

The reflectances of standard white coatings containing 17% (PVC) of $TiO_2$ at thickness between 28 μm and 163 μm were measured and are given in *Table* 3 and *Figures* 1-2.

It is shown that the reflectance of coating depends upon the film thickness. The reflectance rises gradually with the increasing thickness of the film. Moreover, when the thickness exceeds 134 μm, the reflectance reaches 0.93 and gets constant. The reason is that part of the incident radiation transmits the film as the coating film is thin. The thicker the coating film, the less radiation transmits, the higher the reflectance value. When the film is thick enough, the radiation cannot transmit any more. Namely, the incident radiation is absorbed and reflected completely. The "infinitely thick" film is characterized by the fact that any further increase in the thickness does not produce any change in the reflectance. Thus, as long as the thickness of the coating film exceeds 134 μm, the radiation would not transmit the white titanium dioxide coating, so the white $TiO_2$ coating film with thickness more than 134 μm can be considered as an opaque film, for which the sum of reflectance and absorptance is unity.

In this article, the white $TiO_2$ coating film at thickness more than 134 μm with reflectance constant 0.93 is used as a dispersion medium for colored pigments and as a reference for judging the colored pigments absorptivities.

### Measuring Principle for Absoptances of Colored Pigments

As has been shown previously, the transmitted radiation can be ignored for opaque film. That is to say, the incident radiation intensity equals the sum of the reflected and absorbed radiation, namely, $I_0=I_A+I_R$. Here, $I_0$ is the incident light intensity, which equals the reflected intensity of the white film on the premise of regardlessness of absorption; $I_A$ is the absorbed radiation intensity; $I_R$ is the reflected radiation intensity.

If white opaque coating film is considered as dispersion medium, and colored pigments as dispersed substance and reflected radiation intensity at a certain thickness is $I$, it can be depicted in *Figure* 3 and formulated mathematically as follows:

$$-dI \propto Idl \quad (1)$$

where $l$ is thickness of incident radiation.

$$\frac{dI}{I} = -k_1 dl \quad (2)$$

**Table 3—Reflectances (R) of the White Coatings with Different Thickness**

| No. | Thickness (μm) | R |
|---|---|---|
| 1 | 28 | 0.77 |
| 2 | 50 | 0.83 |
| 3 | 78 | 0.86 |
| 4 | 124 | 0.92 |
| 5 | 134 | 0.93 |
| 6 | 163 | 0.93 |

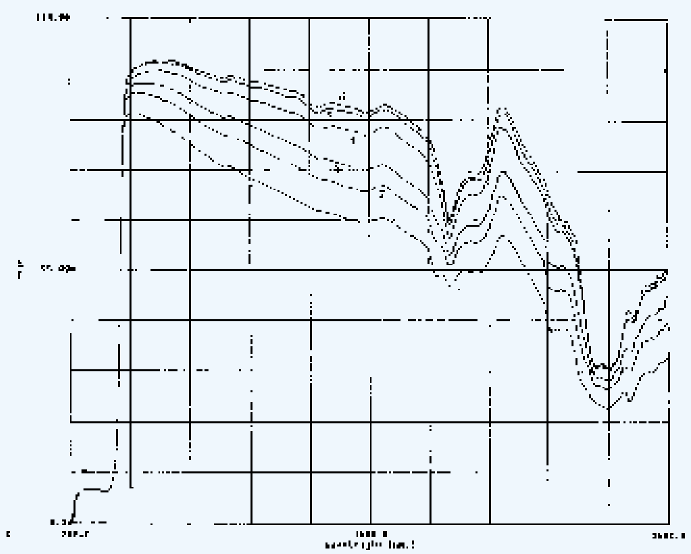

*Figure 1—Reflectance spectra of different thick coatings of $TiO_2$-pigmented coatings.*

Integrate between limits $I_0$ and $I_R$, 0 and $l$:

$$\int_{I_0}^{I_R} \frac{dI}{I} = -k_1 \int_0^l dl \qquad (3)$$

$$\ln \frac{I_R}{I_0} = -k_1 l \qquad (4)$$

Usually the equation is written with base-10 logarithms, which changes simply the constant:

$$\lg \frac{I_0}{I_R} = k' l \qquad (5)$$

$k'$: a coefficient, which relates to the coating temperature, concentration of colored pigment, and wavelength of incident radiation.

For the same incident radiation, if pigment particles can reflect or absorb the light independently, when the concentration of absorbing pigment increases $dc$, the intensity of the reflected radiation will decrease $dl$. Thus,

$$-dl \propto Idc \qquad (6)$$

$$\frac{dI}{I} = -k_2 dc \qquad (7)$$

Upon integration between limits $I_0$ and $I_R$, 0 and $c$:

$$\int_{I_o}^{I_R} \frac{dI}{I} = -k_2 \int_0^c dc \qquad (8)$$

$$\ln \frac{I_R}{I_o} = -k_2 c \qquad (9)$$

In the same way, the equation is written with base-10 logarithms,thus,

$$\lg \frac{I_o}{I_R} = k''c \qquad (10)$$

$k''$: a coefficient, which relates to the coating temperature, thickness, and wavelength of incident radiation. As the thickness and concentration are changeable, equation (11) can be obtained naturally.

$$\lg \frac{I_o}{I_R} = \varepsilon cl \quad \text{or} \quad \lg \frac{1}{R} = \varepsilon cl \qquad (11)$$

In which, $I_0/I_R$ is reciprocal of $R$. ε is absorption coefficient, which relates to the temperature of coating and wavelength of incident radiation. If $A_R = \lg \frac{I_o}{I_R}$, the plot of $A_R$ versus concentration $c$, namely volume ratio of pigment($V_{colored}/V_{TiO_2} \times 100$), should be a straight line, and absorption coefficient ($\varepsilon$) of colored pigment can be gotten from the slope ($s$) of the straight line and the thickness ( $l$ ) of opaque coating: ε = s/l.

## Experimental Conclusions about Colored Pigments Absorptances

In order to test and verify the above inferences, three kinds of pigments (perylene black, toluidine red, benzidine yellow) were mixed respectively with $TiO_2$ at different concentration in white $TiO_2$ reference coating. The thickness values of these coatings were more than 140 µm. Then, the reflectances of colored coatings were measured and shown in *Table* 4.

From *Table* 4 it can be concluded that the reflectances decrease or that absorptances increase with increasing colored pigments concentrations. The plots of $\lg {}^1/_R$ against

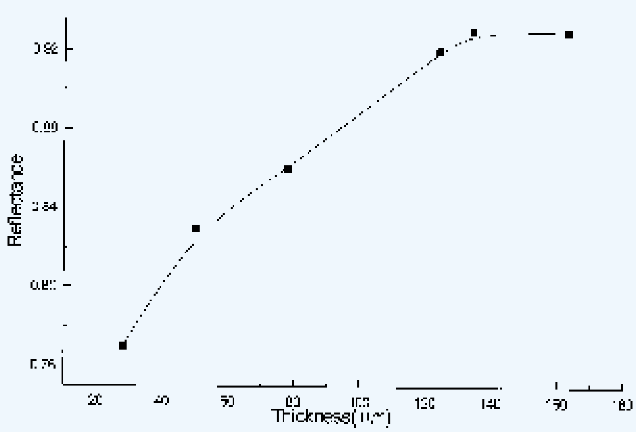


*Figure 2—Solar reflectance of $TiO_2$-pigmented coating as a function of film thickness.*

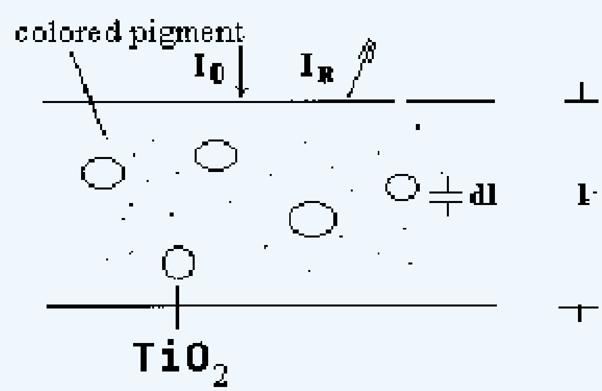


*Figure 3—Reflection and adsorption sketch map of coatings.*

**Table 4—Reflectances of Colored Coatings at Various Colored Pigments Concentrations ($V/V_{TiO2}$)**

| Colored Pigments | No. | $V/V_{TiO2}$ X 100 | R |
|---|---|---|---|
| Perylene black | B1 | 1.12 | 0.756 |
| | B2 | 2.27 | 0.726 |
| | B3 | 3.15 | 0.700 |
| | B4 | 3.85 | 0.678 |
| | B5 | 4.55 | 0.657 |
| | B6 | 5.24 | 0.653 |
| | B7 | 7.27 | 0.646 |
| | B8 | 13.99 | 0.644 |
| Toluidine red | R1 | 1.12 | 0.828 |
| | R2 | 2.50 | 0.813 |
| | R3 | 3.50 | 0.810 |
| | R4 | 4.50 | 0.799 |
| | R5 | 6.00 | 0.798 |
| | R6 | 11.00 | 0.789 |
| Benzidine yellow | Y1 | 1.12 | 0.857 |
| | Y2 | 2.50 | 0.849 |
| | Y3 | 3.50 | 0.840 |
| | Y4 | 4.50 | 0.829 |
| | Y5 | 6.00 | 0.828 |
| | Y6 | 11.00 | 0.817 |

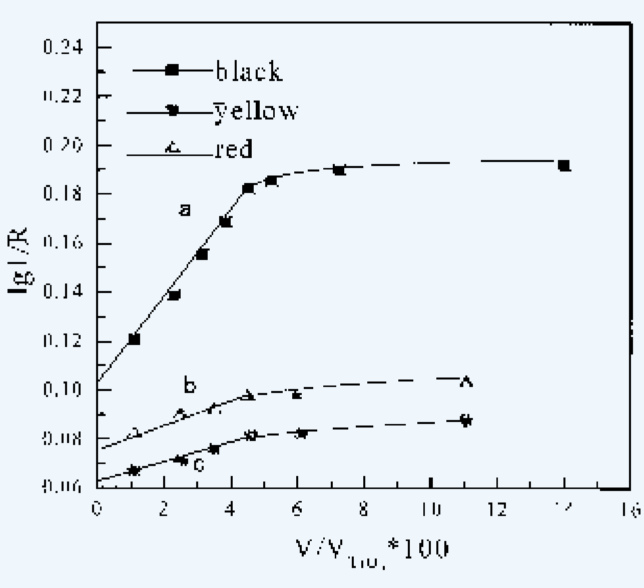


*Figure 4—lg $^1/_R$ versus concentrations of colored pigments.*

$^{V_{colored}}/_{V_{Ti02}} \times 100$ are shown in *Figure* 4.

The conclusion drawn from these curves is:

(1) In the range of low concentration $^{V_{colored}}/_{V_{Ti02}} < 5\%$, the plots of $\lg {}^1/_R$ against concentrations of colored pigments are some straight lines of increasing slopes and conform to equation (11). It can be explained as follows: when the concentration of colored pigment is low, the individual particles are so far apart that each of them can reflect or absorb the radiation independently. In other words, the proportionality between the absorptance and the pigment volume level only applies in the range of low pigment concentrations. At higher pigment levels, because of the shorter and shorter distance between the pigment particles, dependent light scattering arises, which may be interpreted as saying that the particles hinder one another in their light scattering. Consequently, deviations from linearity occur.

(2) Slopes, intercepts and $R_0$ values of linear parts of three curves are shown in *Table* 5, where $R_0$ represents the coating maximum reflectance when the curves extrapolated to zero concentration.

From *Table* 5, linear part of curve (a) gives intercept 0.102. It showed that the coating reflectance is 0.79 (namely, $\lg\frac{1}{0.79} = 0.102$), when the concentration of perylene black is zero. Referring to *Table* 3, it can be seen that the corresponding thickness of white coating with reflectance 0.79 is approximately 40 μm . It indicates that the absorption of black pigment cuts the path of incident radiation down to 40 μm.

Similarly, the intercepts of curve (b) and (c) shown in *Table* 5 are 0.076 and 0.064, respectively, which stand for the coatings reflectance values of 0.84 and 0.86 when the concentrations of colored pigments are zero. Estimated by the same way, the maximum light paths ($l_{max}$) of red coating and yellow coating are approximately 60 μm and 78 μm, respectively.

(3) From the slopes of the linear parts of three curves ($s_{black}$=1.76, $s_{red}$=0.48,

**Table 5—Slopes, Intercepts and $R_0$ Values of Linear Parts of Three Curves**

| Plots | Intercepts | Slopes | $R_0$ |
|---|---|---|---|
| a | 0.102 | 1.76 | 0.79 |
| b | 0.076 | 0.48 | 0.84 |
| c | 0.064 | 0.41 | 0.86 |

**Table 6—Maximum Light Paths and Absorption Coefficients of Three Kinds of Colored Pigments**

| Pigments | $l_{max}$ (μm) | $\varepsilon$(μm$^{-1}$) |
|---|---|---|
| Perylene black | 40 | 0.044 |
| Toluidine red | 60 | 0.0080 |
| Benzidine yellow | 78 | 0.0053 |

$s_{yellow}$=0.41), $l_{max}$ and equation (11), the absorption coefficients can be calculated. After calculation, the absorption coefficient of perylene black is the highest ($\varepsilon_{black}$=0.044 μm$^{-1}$), toluidine red is the second ($\varepsilon_{red}$=0.0080 μm$^{-1}$), and benzidine yellow is the lowest ($\varepsilon_{yellow}$=0.0053 μm$^{-1}$). The maximum light paths and absorption coefficients of three kinds of colored pigments are shown in *Table* 6.

## CONCLUSIONS

Under certain temperatures and in the 250~2500nm spectral region, when $V_{colored}/V_{TiO2}$ is lower than 5%, $A_R$ is in direct proportion to the concentration of colored pigment. From slopes and intercepts, absorption coefficients of colored pigments and maximum light paths of incident radiation can be obtained. This empirical and convenient method, which can be used for quantitative characterization of the pigments absorption coefficients to solar radiation, may be of great help in selecting raw materials and manufacturing tailored solar radiation coatings.

### References

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