3.1 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 [2]. 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 1500-2000 nm seen for W03 and W04. These last two samples are undiluted and 12:1 diluted versions of the same artist color.

Of the available white pigments, the rutile phase of TiO$_2$ has the highest refractive index in the visible (about 2.7) and therefore has the strongest visible light scattering power at the optimum particle size of about 0.2 $\mu$m. Its angle-weighted scattering coefficient $s$ is estimated from the Mie scattering theory to be about 12 $\mu$m$^{-1}$ for the center of the visible spectrum at 550 nm, assuming 0.22 $\mu$m diameter particles suspended in a clear binder with refractive index 1.5 [8, 9]. Based on the same method as [8], one of us [10, Fig. 1 and Eq. (1)] has obtained angle-weighted scattering coefficient $s \approx 10.4$ $\mu$m$^{-1}$ at 550 nm, using slightly different values for the refractive index of TiO$_2$. Thus there is good general agreement among different authors on this basic result from the Mie theory.

The question arises, what is the relation between the Mie theory result for $s$ and the Kubelka-Munk backscattering coefficient $S$? Palmer et al. [8] give an equation for the film reflectance of a non-absorbing layer as $R = (sf\delta)/(2 + sf\delta)$, where $f$ is the pigment volume concentration and $\delta$ is the film thickness. The corresponding Kubelka-Munk equation is $R = S\delta/(1 + S\delta)$, which suggests that $S$ should be identified with $\frac{1}{2}fs$. For clarification, we consider the special case of isotropic scattering, and examine the limit of weak scattering. Then $s$ is just the total scattering cross section. In this limit the result of Palmer et al. is exact if the incident radiation is a normally incident collimated beam; half the scattering is into the forward hemisphere, and half into the backward hemisphere. However, we are more interested in the reflectance for completely diffuse radiation, which is twice as large in this limit. Thus we identify $S$ with $fs$. Superimposed on the backscattering curves for samples W01 - W04 are additional Mie-theory estimates for backscattering coefficient $S$ as a function of wavelength, based on Ref. [10, Fig. 1 and Eq. (1)]. The measurements and theoretical estimates are in reasonable, but not precise, agreement.

At the longer infrared wavelengths, the measured backscattering declines more slowly than the theoretical values. (The theoretical values are approaching a Rayleigh regime in which $S$ is proportional to the inverse fourth power of wavelength.) A plausible reason is the clumping of pigment particles. It is known that such clumping can raise the near-infrared reflectance [11].

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 [12].

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 four 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 polyester substrate.
References


