3.3 Blue/Purple

3.3.1 Cobalt Aluminate Blue, Cobalt Chromite Blue

Cobalt aluminate blue (nominally $CoAl_2O_4$, but usually deficient in Co [3]; **U01 - U05**) and cobalt chromite blue ($Co[Al,Cr]_2O_4$; **U06 - U09**) derive their appearances from modest scattering ($S \approx 30$ mm^{-1}) in the blue (400 - 500 nm) and strong absorption ($K \approx 150$ mm^{-1}) in rest of the visible spectrum. They have very low absorption in the short NIR, but exhibit an undesirable absorption band in the 1200 - 1600 nm range, which contains 17% of the NIR energy. A white background dramatically increases NIR reflectance but makes some (e.g., cobalt aluminum blue spinel U02) much lighter in color.

3.3.2 Iron Blue

Iron (a.k.a. Prussian or Milori) blue (**U10**) is a weakly scattering pigment with strong absorption in the visible and short NIR, and weak absorption at longer wavelengths. It appears black and has little NIR reflectance over a black background, but looks blue and has achieves a modest NIR reflectance (0.25) over a white background. It is not ideal for cool coating formulation.

3.3.3 Ultramarine Blue

Ultramarine blue (**U11**), a complex silicate of sodium and aluminum with sulfur, is a weakly scattering pigment with some absorption in the short NIR. If sparingly used, it can impart absorption in the yellow spectral region without introducing a great deal of NIR absorption. This is a durable inorganic pigment with some sensitivity to acid [2].

While most colored inorganic pigments contain a transition metal such as Fe, Cr, Ni, Mn, or Co, ultramarine blue is unusual. It is a mixed oxide of Na, Si, and Al, with a small amount of sulfur ($Na_{7.5}Si_6Al_6O_{24}S_{4.5}$). The metal oxide skeleton forms an open clathrate sodalite structure that stabilizes S_3^- ions in cages to form the chromophores [3, section 3.5] [20]. Thus isolated S_3 molecules with an attached unpaired electron cause the light absorption in the 500-700 nm range, producing the blue color. The refractive index of ultramarine blue is not very different from the typical matrix value of 1.5 [3, section 3.5], so the pigment causes little scattering.

3.3.4 Phthalocyanine Blue

Copper phthalocyanine blue (**U12 - U13**) is a weakly scattering, dyelike pigment with strong absorption in the 500 - 800 nm range and weak absorption in the rest of the visible and NIR. Phthalo blue appears black and has minimal NIR reflectance over a black background, but looks blue and achieves a high NIR reflectance (0.63) over a white background (U12). It is durable and lightfast, but as an organic pigment it is less chemically stable than (high temperature) calcined mixed metal oxides such as the cobalt aluminates and chromites. General information on the structure and properties of phthalocyanines is available in [21]. The refractive index varies with wavelength, and exceeds 2 in the short wavelength part of the infrared spectrum [22]. Therefore the weak scattering we observe in our samples indicates that the particle size is quite small. The pigment handbook indicates a typical particle diameter of 120 nm [2], which is consistent with our data.

3.3.5 Dioxazine Purple

Dioxazine purple (**U14**) is an organic optically similar to phthalo blue, but even more absorbing in the visible and less absorbing in the NIR. It is nearly ideal for formulation of dark NIR-transparent layers, but is subject to the chemical stability considerations noted above for phthalo blue.

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