3.2 Black/Brown

3.2.1 Carbon Black, Other Non-Selective Black

Carbon black, bone black (10% carbon black + 84% calcium phosphate), copper chromite black ($CuCr_2O_4$), and synthetic iron oxide black (Fe_3O_4 magnetite) (**B01 - B04**) are weakly scattering pigments with strong absorption across the entire solar spectrum. Carbon black B01 is the most strongly absorbing, but all four are "hot" pigments.

Most non-selective blacks are metallic in nature, with free electrons permitting many different allowed electronic transitions and therefore broad absorption spectra. Carbon black is a semi-metal that has many free electrons, but not as many as present in highly conductive metals. Both the iron oxide (magnetite) and copper chromite blacks are (electrically conducting) metals.

3.2.2 Chromium Iron Oxide Selective Black

Chromium iron oxide selective blacks (**B05 - B11**) are mixed metal oxides (chromium green-black hematite, chromium green-black hematite modified, chromium iron oxide, or chromium iron nickel black spinel) formulated to have NIR reflectance significantly higher than carbon and other non-selective blacks. Some, such as chromium green-black hematite B06, appear more brown than black. While these pigments have good scattering in the NIR, with a backscattering coefficient at 1000 nm about half that of TiO_2 white, they are also quite absorbing ($K \approx 50$ mm^{-1}) in the short NIR. These pigments are visibly hiding (opaque to visible radiation) and NIR transmitting, so use of a white background improves their NIR reflectances without significantly changing their appearances.

Pure chromium oxide green (Cr_2O_3), pigment green 17, has the hematite crystal structure and will be discussed further together with other green pigments. When some of the chromium atoms are replaced by iron, a dark brownish black with the same crystal structure is obtained—i.e., a traditional cool black pigment (e.g., B06-B11; B05 differs because it contains nickel and has a spinel structure). It is sometimes designated as Cr-Fe hematite [13] or chromium green-black hematite [14], and has been used to formulate infrared-reflective vinyl siding since about 1984 [15]. A number of modern recipes for modified versions of this basic cool black incorporate minor amounts of a variety of other metal oxides. One example is the use of a mixture of 93.5 g of chromium oxide, 0.94 g of iron oxide, 2.38 g of aluminum oxide, and 1.88 g of titanium oxide [16]. The mixture is calcined at about 1100°C to form hematite-structure crystallites of the resulting mixed metal oxide.

3.2.3 Organic Selective Black

Perylene black (**B12**) is a weakly scattering, dyelike organic pigment that absorbs strongly in the visible and very weakly in the NIR. Its sharp absorption decrease at 700 nm gives this pigment a jet black appearance and an exceptionally high NIR reflectance (0.85) when applied over white. Perylene pigments exhibit excellent lightfastness and weatherfastness, but their basic compound (dianhydride of tetracarboxylic acid) may or may not be fast to alkali; references [4] and [2] disagree on the latter point.

3.2.4 Iron Oxide Brown

Iron oxide browns (**B13 - B15**) such as burnt sienna, raw sienna, and raw umber exhibit strong absorption in part of the visible spectrum and low absorption in the NIR. These can provide effective cool brown coatings if given a white background, though this will make some (e.g., burnt sienna B13) appear reddish. These browns are "natural" and can be expected to contain various impurities.

3.2.5 Other Brown

Other browns characterized (**B16 - B21**) include iron titanium (Fe-Ti) brown spinel, manganese antimony titanium buff rutile, and zinc iron chromite brown spinel. These mixed-metal oxides have strong absorption in most or all of the visible spectrum, plus weak absorption and modest scattering in the NIR. A white undercoating improves the NIR reflectance of all browns, but brings out red tones in iron titanium brown spinels B16 and B17.

The cool Fe-Ti browns (B16 - B18) have spinel crystal structure and basic formula Fe_2TiO_4 [14, 17]. Despite the presence of Fe^{2+} ions, the infrared absorption of this material is weak. (In many materials, the Fe^{2+} ion is associated with infrared absorption [18, 19]; see also our data for Fe_3O_4. The current data demonstrate that the absorption spectra also depend on the environment of the Fe^{2+} ion.) We also note that while B17 and B18 are nominally the same material, the details of the absorption are different.

We have not yet characterized a synthetic iron oxide hydrate brown (e.g., FeOOH).

References

[1] Ronnen Levinson, Paul Berdahl, and Hashem Akbari. Solar spectral optical properties of pigments, Part I: model for deriving scattering and absorption coefficients from transmittance and reflectance measurements. *Solar Energy Materials & Solar Cells (accepted)*, 2004.

[2] Peter A. Lewis. *Pigment Handbook*, volume I. John Wiley and Sons, 1988.

[3] Gunter Buxbaum. *Industrial Inorganic Pigments*. Wiley-VCH, 2nd edition, 1998.

[4] Willy Herbst and Klaus Hunger. *Industrial Organic Pigments*. VCH, 1993.

[5] Y.S. Touloukian, D.P. DeWitt, and R.S. Hernicz. *Thermal Radiative Properties: Coatings*, volume 9 of *Thermophysical Properties of Matter*. IFI/Plenum, 1972.

[6] Ralph Mayer. *The Artist's Handbook of Materials and Techniques*. Viking Penguin, 5th edition, 1991.

[7] Society of Dyers and Colourists and American Association of Textile Chemists and Colorists. Colour index international: Fourth online edition. *http://www.colour-index.org*.

[8] B. R. Palmer, P. Stamatakis, C. G. Bohren, and G. C. Salzman. A multiple-scattering model for opacifying particles in polymer films. *Journal of Coatings Technology*, 61(779):41–47, 1989.

[9] E.S. Thiele and R.H. French. Computation of light scattering by anisotropic spheres of rutile titania. *Adv. Mater.*, 10(15):1271–1276, 1998.

[10] Paul Berdahl. Pigments to reflect the infrared radiation from fire. *Journal of Heat Transfer*, 117:355–358, May 1995.

[11] D.J. Rutherford and L.A. Simpson. Use of a floculation gradient monitor for quantifying titanium dioxide pigment dispersion in dry and wet paint films. *Journal of Coatings Technology*, 57(724):75–84, May 1985.

[12] R.R. Blakey and J.E. Hall. *Pigment Handbook*, volume I, chapter A ("Titanium Dioxide"), pages 1–42. John Wiley and Sons, 1988.

[13] Daniel Russell Swiler. Manganese vanadium oxide pigments. U.S. Patent 6,485,557 B1, Nov 26 2002.

[14] Dry Color Manufacturer's Association (DCMA). *Classification and chemical description of the complex inorganic color pigments*. Dry Color Manufacturer's Association, P.O. Box 20839, Alexandria, VA 22320, 1991.

[15] E. B. Rabinovitch and J. W. Summers. Infrared reflecting vinyl polymer compositions. U.S. Patent 4,424,292, 1984.

[16] Terrence R. Sliwinski, Richard A. Pipoly, and Robert P. Blonski. Infrared reflective color pigment. U.S. Patent 6,174,360 B1, Jan 16 2001.

[17] V.A.M. Brabers. The electrical conduction of titanomagnetites. *Physica B*, 205:143–152, 1995.

[18] L.B. Glebov and E.N. Boulos. Absorption of iron and water in the Na_2O-CaO-MgO-SiO_2 glasses, II. Selection of intrinsic, ferric, and ferrous spectra in the visible and UV regions. *J. Non-Crystalline Solids*, 242:49–62, 1998.

[19] R.N. Clark. *Manual of Remote Sensing*, volume 3 ("Remote sensing for the earth sciences"), chapter 1 ("Spectroscopy of Rocks and Minerals, and Principles of Spectroscopy", pages 3–58. John Wiley and Sons, http://speclab.cr.usgs.gov, 1999. Fig. 5.

[20] R.J.H. Clark and D.G. Cobbold. Characterization of sulfur radical anions in solutions of alkali polysulfides in dimethylformamide and hexamethylphosphoramide and in the solid state in ultramarine blue, green, and red. *Inorganic Chemistry*, 17:3169–3174, 1978.

[21] N.B. Mckeown. *Phthalocyanine Materials: Synthesis, Structure and Function*. Cambridge Univ. Press, Cambridge, UK, 1998.

[22] S. Wilbrandt O. Stenzel A. Stendal, U. Beckers and C. von Borczyskowski. The linear optical constants of thin phthalocyanine and fullerite films from the near infrared to the UV spectral regions: estimation of electronic oscillator strength values. *J. Phys. B*, 29:2589–2595, 1996.

[23] D. de Cogan and G.A. Lonergan. Electrical conduction in Fe_2O_3 and Cr_2O_3. *Solid State Communications*, 15:1517–1519, 1974.

[24] Hamnett Goodenough. *Landolt-Bornstein Numerical Data and Functional Relationships in Science and Technology, New Series, Group III: Crystal and Solid-State Physics*, volume 17g (Semiconductors: Physics of Non-Tetrahedrally Bonded Binary Compounds III), chapter 9.15.2.5.1: Oxides of chromium, pages 242–247,548–551. Springer-Verlag, Berlin, 1984.

[25] G.B. Smith, A. Gentle, P. Swift, A. Earp, and N. Mronga. Coloured paints based on coated flakes of metal as the pigment, for enhanced solar reflectance and cooler interiors: description and theory. *Solar Energy Materials & Solar Cells*, 79(2):163–177, 2003.

[26] G.B. Smith, A. Gentle, P. Swift, A. Earp, and N. Mronga. Coloured paints based on iron oxide and solicon oxide coated flakes of aluminium as the pigment, for energy efficient paint: optical and thermal experiements. *Solar Energy Materials & Solar Cells*, 79(2):179–197, 2003.