

5

Complex Inorganic Color Pigments: An Overview.

James White

5.1

Introduction

An important family of high performance pigments is termed complex inorganic color pigments, or CICPs. Chemically, these pigments are synthetic crystalline metal oxides that have structures identical to those of naturally occurring minerals. They are called complex because they contain two or more different metals^[1]. Complexity provides a range of metal combinations and in practice gives a wide range of colors for this class of pigments.

CICPs are used when outstanding color stability is required. Resistant to attack and dissolution by chemical agents and solvents, they do not bleed or migrate in application. They have heat stabilities hundreds of degrees higher than organic pigments, and are not discolored by exposure to ultraviolet (UV) light. The fact that these pigments absorb UV light without decomposition makes them good UV absor-

1																	2				
H																	He				
3	4															5	6	7	8	9	10
Li	Be															B	C	N	O	F	Ne
11	12															13	14	15	16	17	18
Na	Mg															Al	Si	P	S	Cl	Ar
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36				
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr				
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54				
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe				
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86				
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn				
87	88	89	104	105	106	107	108	109	110	111	112										
Fr	Ra	Ac*	Rf	Db	Sg	Bh	Hs	Mt													
58	59	60	61	62	63	64	65	66	67	68	69	70	71								
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lw								
90	91	92	93	94	95	96	97	98	99	100	101	102	103								
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr								

Figure 5-1: Elements commonly found in CICPs. Light shaded elements are those responsible for the primary color. Dark shaded elements are colorless and are present to balance charge and to modify color hues.

bers and opacifiers in their own right. They are the most stable and durable type of colorants commercially available – truly high performance products.

The elements typically found in CICPs are listed in Figure 5–1. Of these metal ions, only seven, all transition metals, are responsible for producing color^[2]. Other metal ions in the pigments are colorless, and are added as modifiers to balance the charge of the crystal lattice, or to slightly modify the shade that the coloring ions produce.

Transition metal compounds are generally quite colorful, and CICPs are no exception. Color in CICPs is generated by electronic d–d transitions on the coloring metal ions in the crystal lattice, or from metal-to-conduction band transitions within the solids. These metal-based electronic transitions are spectroscopically unfavorable, resulting in relatively poor light absorption^[3]. This means that CICPs have relatively weak coloring power when compared to other pigments. However, metal oxides are very stable entities and their color is very durable.

5.2

Structures of CICPs

CICPs are metal oxides, which can have a number of possible structures. The biggest determining factor in the structure is the oxygen/metal (O/M) ratio (Table 5–1). As long as the metal ions are of a comparable size, it is the O/M ratio that largely determines what the structure will be. Two crystal structures dominate the class of CICPs – those of rutile and spinel. The hematite and corundum structures are also observed, but are much less common.

Table 5–1: Structures and formulas of common CICPs.

<i>Crystal type</i>	<i>Basic formula</i>	<i>O/M ratio</i>
Rutile	MO ₂	2.00
Hematite or corundum	M ₂ O ₃	1.50
Spinel	M ₃ O ₄	1.33

Rutile is the name of one of the crystalline phases of the mineral titanium dioxide, TiO₂. It is the most dense phase of naturally occurring titanium dioxide, with a stoichiometry of 2 oxygens to 1 metal, or O/M = 2. Formulations containing metal ions of similar size to Ti(IV) with an O/M ratio of 2 will often adopt the rutile structure. CICPs with this structure contain a large fraction of TiO₂ as a base oxide. Not surprisingly, rutile CICPs have many physical properties in common with titanium dioxide. Metal ions in rutile are octahedrally coordinated by six oxygen ions, as shown in Figure 5–2.

The spinel structure, named from the mineral spinel, MgAl₂O₄, is very common for many of the first row transition metal oxides. It has an O/M ratio of 1.33, and numerous transition metal oxides adopt this structure when they have this M/O ratio. In fact, the structure is so stable that even stoichiometries substantially differ-

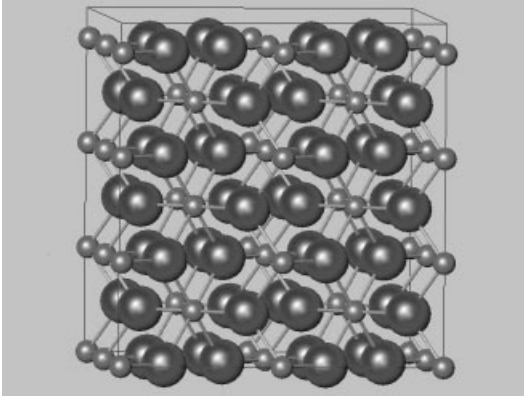


Figure 5-2a: A view of the rutile crystal structure. Oxide ions are large and metal ions are small spheres.

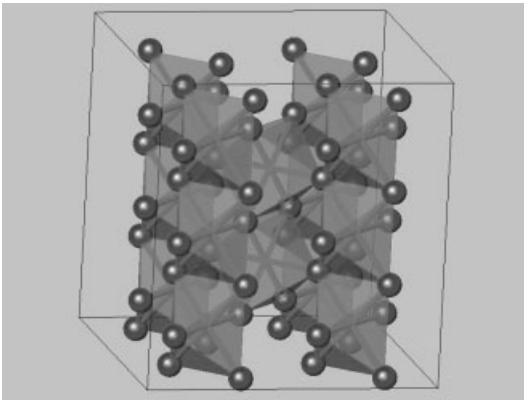


Figure 5-2b: Another view of the rutile structure showing the connectivity of the MO_6 octahedra. Metal ions, removed for clarity, reside at the center of each octahedron.

ent from M_3O_4 can retain the spinel configuration. In these cases, the solids generally contain metal ion vacancies.

The spinel structure contains metal ions in different oxidation states. Generally, there are divalent (+2) and trivalent (+3) metal ions in the structure, although other charged ions can be accommodated. There are two distinct coordination environments for metal ions in spinel. One site is octahedrally coordinated by the oxygen ions, while the other is tetrahedrally coordinated. An example of the spinel lattice showing these sites is displayed in Figure 5-3. Normal spinels have only divalent metal ions in tetrahedral sites and only trivalent metal ions in the octahedral ones. Inverse spinels also occur, where some divalent metal ions are 6-coordinated, with some trivalent ions in 4-coordinated sites.

The other structures of interest are those with the basic formula M_2O_3 , $\text{O}/\text{M} = 1.5$. There are two of these structures found in CICPs, one being corundum, named after the α -alumina phase of Al_2O_3 , and the other is hematite named after the mineral Fe_2O_3 . There is a slight difference in spatial geometry between the two structures, but both are quite similar. Metal ions are trivalent and octahedrally coordinated in both.

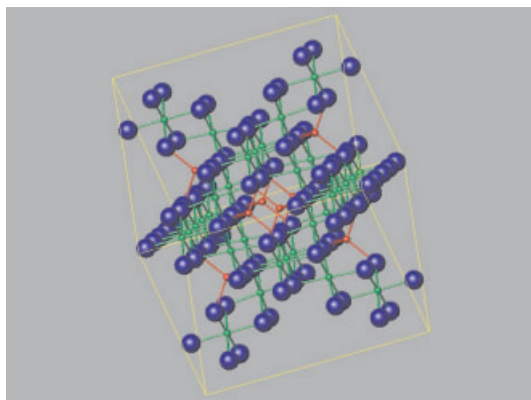


Figure 5–3: A view of the spinel crystal structure. Oxide ions are blue, octahedrally coordinated metals and their bonds are green, and tetrahedrally coordinated metals and their bonds are red. Some atoms and bonds have been removed for clarity.

5.3

Production of CICPs

CICPs are made by calcination (strong heating in air) of blends of metal oxides and/or oxide precursors such as metal salts, hydrates, and carbonates. Calcination temperatures typically range from 650 to 1300 °C. At relatively low temperatures, all the raw ingredients decompose to form the metal oxides. At higher temperatures, this oxide mix becomes reactive. Metal and oxide ions become mobile and interdiffuse to create a homogeneous solid. The ions in the solid then rearrange to a stable crystalline structure that is determined by the metals present, the O/M ratio, and the calcining temperature. This new structure is the color pigment. Following calcination, CICPs are milled to achieve a specific particle size, often washed, and finally blended for uniformity.

Three main groups of CICPs are commercially produced. Titanates, which use a titanium dioxide base, aluminates, which use an aluminum oxide base, and chromites and ferrites, which have chromium and/or iron oxide bases.

5.4

Titanate Pigments

Titanate-based pigments contain titanium dioxide as a base component. The different types are listed in Table 5–2^[4]. Pigments using TiO₂ as a modifier are not included here. The important crystalline types are rutiles and spinels, with few other structures having commercial relevance. Titanates comprise the largest volume of CICPs in use today, and of these the greatest usage is of the rutile grades. Detailed information on titanate pigments can be found in Chap. 7 of this volume.

Table 5–2: Common titanate-based CICPs.

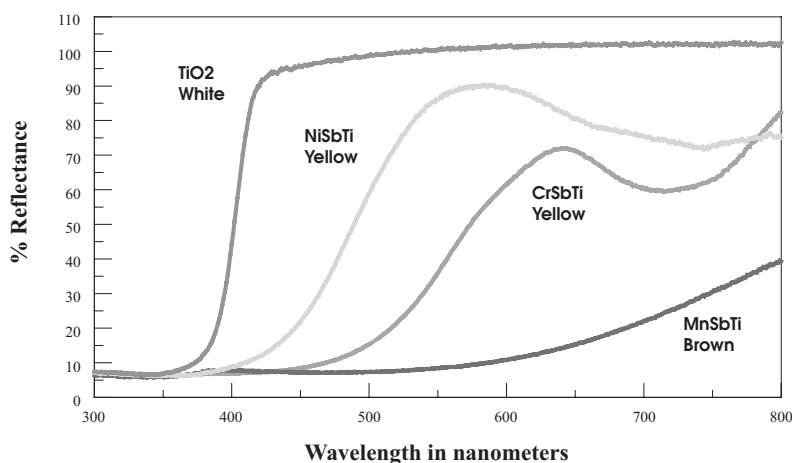
<i>Chemical type</i>	<i>C.I. Pigment</i>	<i>Color</i>	<i>Crystal Type</i>
CoTi	Green 50	Green	Spinel
BaNiTi	Yellow 157	Yellow-green	Priderite
NiSbTi	Yellow 53	Yellow	Rutile
NiNbTi	Yellow 161	Yellow	Rutile
NiWTi	Yellow 189	Yellow	Rutile
CrSbTi	Brown 24	Yellow-orange	Rutile
CrNbTi	Yellow 162	Yellow-orange	Rutile
CrWTi	Yellow 163	Orange	Rutile
FeTi	Black 12	Yellow-brown	Spinel
MnSbTi	Yellow 164	Brown	Rutile
MnNbTi	Brown 37	Brown	Rutile
MnCrSbTi	Brown 40	Brown	Rutile
MnWTi	Brown 45	Brown	Rutile

5.4.1

Rutile Titanates

Rutile titanates represent by far the largest commercial class of CICPs. Chromium antimony titanate yellows (C.I. Pigment Brown 24) are the most widely used, followed by nickel antimony titanate yellows (C.I. Pigment Yellow 53). Manganese antimony titanate browns (C.I. Pigment Yellow 164) occupy a much smaller market share, and the other rutile grades a significantly smaller fraction still.

Rutile CICPs contain a significant amount of titania as a base oxide. Typically they range from 70 to 90 % TiO_2 by pigment weight. Transition metal cations Ni(II), Cr(III), and Mn(III) are responsible for producing the color, while the colorless ions

Figure 5–4: Reflectance spectra of selected rutile CICPs compared to rutile TiO_2 .

Ti(IV), Sb(V), Nb(V), and W(VI) are present to maintain the MO_2 stoichiometry. Colors range from light yellow to dark brown. Reflectance curves for the three antimony titanates are compared to rutile TiO_2 in Figure 5–4.

It is well known that pure rutile titanium dioxide has a photoactive surface^[5, 6]. When irradiated with UV light, highly reactive oxo radicals are formed that can photocatalytically degrade organic materials in contact with the pigment's surface. Commercial grades of rutile TiO_2 are passivated with coatings of other metal oxides such as those of aluminum, silicon, or zirconium to suppress this effect.

Rutile CICPs do not exhibit photocatalytic activity as do pure titanium dioxides. The act of doping the rutile structure with the transition metal and other ions eliminates the mechanism for formation of surface radicals via UV irradiation. Commercial grade rutile CICPs do not require surface coatings to make them inert.

5.4.2

Spinel Titanates

Titanate spinels form a much smaller class of pigments than the rutiles. The M_3O_4 stoichiometry of spinel is met by reacting two units of +2 metal oxide with one unit of TiO_2 , according to Eq. (5–1).



Titanates are inverse spinels, where a number of the +2 ions occupy octahedral coordination sites in the lattice. Commercially important grades are the cobalt titanate greens and iron titanate browns.

Cobalt titanate greens are generally modified by Zn(II) and Ni(II) oxides to produce their bright green colors. The greens can be in the same color space as chromium(III) oxide green, and compete somewhat since they have similar durability characteristics. However, cobalt titanate greens are usually formulated to give brighter and cleaner colors shades, some with bluer hues that are not otherwise available. Primarily as a result of the cobalt they contain, cobalt titanate greens are more expensive by comparison.

Iron titanates are formed from combinations of iron(II) oxide and TiO_2 . These formulations are commonly modified by additions of iron(III) oxide, zinc(II) oxide, and aluminum(III) oxide. Like the cobalt titanates, these are inverse spinels structures. Iron titanate pigments yield light yellow-brown to dark reddish-brown hues. In many cases these pigments exhibit greater heat stability than zinc ferrite or iron oxide browns, and are generally used in applications for this purpose.

5.4.3

Other Titanates

The only other commercially important grade of titanate pigment, besides those listed above, is barium nickel titanium yellow priderite. The name priderite, just as with spinel and rutile above, refers to the crystal structure of this compound. These

pigments provide a lighter, greener shade of yellow than is typically common for nickel titanate yellows. With that exception, other properties are similar to those of other CICPs. Yellow priderite has the basic formula $2\text{NiO} \times 3\text{BaO} \times 17\text{TiO}_2$.

5.5

Aluminate Pigments

CICPs that contain aluminum oxide, Al_2O_3 , or alumina as a colorless base oxide are called aluminates. These almost always employ cobalt(II) oxide, CoO , as one of the coloring oxides. All of these pigments adopt the spinel crystal structure, and all have color hues in the blue to teal range.

5.6

Cobalt Aluminates

Combinations of cobalt(II) oxide and aluminum oxide in the spinel stoichiometry give cobalt aluminate blue spinels, CoAl_2O_4 , C.I. Pigment Blue 28. Variations of this pigment include modification by zinc (C.I. Pigment Blue 72), magnesium, titanium, and lithium oxides. If lithium and titanium modifiers are added, a turquoise blue pigment is obtained.

Table 5–3: Common aluminate-, chromite-, and ferrite-based CICPs.

<i>Chemical type</i>	<i>C.I. Pigment</i>	<i>Color</i>	<i>Crystal Type</i>
CoAl	Blue 28	Blue	Spinel
CoCrAl	Blue 36	Blue-green to teal green	Spinel
CoCr	Green 26	Dark green	Spinel
ZnFe	Yellow 199	Yellow-brown	Spinel
	Brown 31	Yellow-brown	Spinel
MgFe	Brown 11	Red-brown	Spinel
ZnCrFe	Brown 33	Brown	Spinel
FeCr	Green 17	Brown-black	Hematite/corundum
	Brown 29		
FeCr	Brown 35	Brown-black	Spinel
CuCrFe	Black 23	Black	Spinel
FeMn	Black 26	Black	Spinel
CoCrFe	Black 27	Black	Spinel
CuCr	Black 28	Black	Spinel
CoFe	Black 29	Black	Spinel
NiCrMn	Black 30	Black	Spinel

Cobalt aluminate blues are the most durable blue pigments commercially available. They have excellent chemical and heat stability, and can be used in chemically aggressive environments and exterior durable applications without color fade. One drawback is that these blues are poor UV absorbers when compared to other CICPs.

5.7

Cobalt Chromium Aluminates

If some of the aluminum oxide in a cobalt aluminate is replaced with chromium(III) oxide green, the resulting compound is a cobalt chromium aluminate blue-green spinel (C.I. Pigment Blue 36), with basic formula $\text{Co}(\text{Al}_x\text{Cr}_{1-x})_2\text{O}_4$, where x ranges from 0 to 1. These pigments can be further modified with zinc, magnesium, and titanium oxides to produce greener blues and teal shades.

Like the cobalt aluminates, cobalt chromium aluminates have excellent heat stability and weatherfastness. In many cases they have significantly better UV opacity than the Pigment Blue 28 grades.

5.8

Chromites and Ferrites

A large number of CICPs contain transition metal oxides without a significant amount of a colorless base oxide. These pigments, listed in Table 5–3, employ either green chromium(III) oxide, red iron(III) oxide, or a combination of the two as a base. They are thus referred to as chromites or ferrites^[7], for the chromium and iron bases, respectively. Most adopt the spinel configuration, with the other important structures being those of corundum and hematite.

Chromite and ferrite pigments have physical properties similar to those of the titanates and aluminates. Nearly all pigments of this variety are of brown and black shades, with just a few greens and green-blues. Some have unique infrared spectral properties that make them of interest in addition to their durability and color stability.

5.9

Black CICPs

There are three types of black chromites and ferrites. These contain copper, cobalt, and nickel. The copper-containing blacks include C.I. Pigments Black 23, Black 26 (modified), and Black 28. Cobalt-containing grades include C.I. Pigments Black 27 and Black 29. There is one important nickel black, C.I. Pigment Black 30. All of these blacks have spinel crystal structures. The copper blacks are the most widely used, as they are excellent general purpose pigments. The cobalt and nickel blacks are used only in applications where their special properties are required.

Copper chromite blacks (C.I. Pigment Black 28) are spinels made from copper(II) oxide and chromium(III) oxide green, with a general formula of CuCr_2O_4 . The presence of copper slightly distorts the usually cubic oxide lattice, and pure copper chromites are tetragonal spinels. The most common modifier in these blacks is manganese, which is present in many commercially available grades. Iron and molybdenum are the other modifiers of note.

Copper chromites are the most widely used CICP blacks. They offer a good jet-black color, excellent durability, and heat stability up to 1000 °C. These blacks are also excellent UV absorbers, and offer good UV opacity to the systems that employ them. Being chemically stable, copper chromite blacks are not prone to photocatalytically decompose in the presence of titanium dioxide white. Because of this, exterior durable grays and dark shaded colors are often formulated using these blacks. High heat systems such as silicone paints and glass enamels use copper chromites to make jet-blacks and grays.

When blacks of greater heat stability than copper blacks are needed, cobalt blacks must be used. Cobalt blacks have the general formula $(\text{Co}_x, \text{Fe}_{1-x})\text{M}_2\text{O}_4$, for $x = 0$ to 1, $\text{M} = \text{Fe}$, or Cr and Fe , and are described as C.I. Pigments Black 29 and Black 27, respectively. Nickel(II) oxide is the most commonly employed modifier. Because they contain a significant amount of cobalt, they are significantly more expensive than other CICP blacks. The higher cost restricts their use to porcelain and glass enamel systems that require the greater heat stability.

The only important nickel blacks are described as C.I. Pigment Black 30, and have the general formula $(\text{Ni}_y, \text{Fe}_{1-y})(\text{Fe}_x, \text{Cr}_{1-x})_2\text{O}_4$, where x and y range from 0 to 1. The commercial grades are commonly modified with Mn(II) and Mn(III) oxides. These pigments are slightly more heat stable than the copper blacks, but not as heat stable as the cobalt blacks. They have a slight brown undertone compared to the

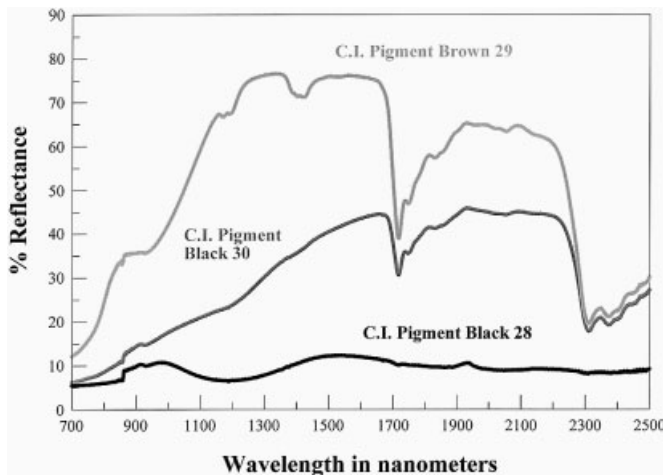


Figure 5-5: Reflectance spectra of two IR-reflective CICPs compared with a non-reflective Pigment Black 28. Dips in reflection centered at 1700 and 2300 nm are due to the polymer matrix.

other CICP blacks. These pigments are most commonly used for their infrared (IR) reflective properties.

In the near IR region, the nickel blacks reflect a significant amount of radiation compared with most other high performance blacks, as shown in Figure 5–5. More reflection causes less IR light to be absorbed. Exterior plastics and coatings pigmented with these blacks will therefore heat to a lesser degree in direct sunlight. Not surprisingly, the largest application for nickel blacks is in exterior coatings and PVC siding and window profiles, where durable color with minimal heating from the sun is desired.

5.10

Brown Pigments

There are three groups of commercially important ferrite and chromite browns. The first are pure ferrites defined by C.I. Pigments Brown 11, Brown 31, and Yellow 119, followed by the mixed chromite/ferrite browns which are C.I. Pigments Brown 33 and Brown 35. These are all spinels. The third type is mixed chromium iron pigments. These pigments adopt either the hematite or the corundum structures.

Pure ferrite spinels containing zinc, C.I. Pigments Yellow 119 and Brown 31, or magnesium, C.I. Pigment Brown 11, provide light yellow-brown to light red-brown colors. Zinc ferrites, and to a lesser extent magnesium ferrites, are widely used as heat-stable colorants for thermoplastics.

The mixed chromite/ferrite spinels, C.I. Pigments Brown 33 and Brown 35, provide darker browns than the pure ferrites, covering the color range from reddish-brown to nearly black. These products are used mainly in plastics and coatings to provide heat stable colors. In addition, Brown 35 spinels have good IR-reflective properties, and are used in low heat build-up plastics and coatings.

Pigments containing only iron(III) and chromium(III) oxides in an M_2O_3 stoichiometry are identified as either C.I. Pigment Green 17 or C.I. Pigment Brown 29. Both of these Colour Index descriptions denote the same pigment type, and the names can be used interchangeably. The pigments are not spinels, as they adopt either the corundum or hematite structures. They are dark red-brown to nearly black in color.

The great feature of these pigments is their good IR reflectivity. They generally have higher IR reflectivity than other dark IR-reflective CICPs, as demonstrated in Figure 5–5. These browns and blacks are primarily used to prepare dark exterior durable colors with low heat build-up.

5.11

Green Chromites

There is one commercially important chromite-based green pigment in this class. This is a cobalt chromite green, C.I. Pigment Green 26. These pigments are spinels made from cobalt(II) oxide and chromium oxide green, with the general formula

CoCr_2O_4 . Common modifiers include aluminum, titanium, magnesium, and zinc oxides. The cobalt(II) ions in the spinel are tetrahedrally coordinated, providing the green chromium oxide base with a bluish hue. Generally these colors range from bright green-blue to a dark forest green.

The major use of cobalt chromite greens is in camouflage applications. In the near IR region (700 to 1000 nm), the pigments exhibit a reflectance similar to that of some natural backgrounds. Cobalt chromites have proved useful in preparing greenish colors that match ambient IR signatures.

References and Notes

- 1 Simple metal oxide colorants are those containing only one type of metal such as iron(III) oxide red, titanium dioxide white, and chromium(III) oxide green, according to this scheme.
- 2 The elements in the periodic table in which the d-electron shell is filled are all metals. These elements are referred to as the transition metals.
- 3 F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 4th edn., 1980, pp. 657–658, John Wiley & Sons, New York.
- 4 Pigment types are commonly referred to by their Colour Index (C.I.) designation, an internationally recognized nomenclature. These names are found in *Colour Index, International Pigments & Solvent Dyes*, Society of Dyers and Colourists, 3rd. edn., 1997, Bradford, West Yorkshire, England.
- 5 Peter A. Lewis, (ed.), *Pigment Handbook*, Vol. 1, Properties and Economics, 2nd edn., 1988, pp. 22–24, John Wiley & Sons, New York.
- 6 Swaraj Paul, *Surface Coatings Science and Technology*, 1985, pp. 324–326, John Wiley & Sons, New York.
- 7 The prefix ferri- in chemistry denotes iron in the +3 oxidation state, as it is in the red iron(III) oxide, Fe_2O_3 . It is derived from the Latin word “ferrum” for iron.