PECHINI METHOD: $ZrO_2 - Fe_2O_3$ PIGMENTS

V. C. Albarici [1], R. C. Lima [1], C. A. Paskocimas [2], E. Longo [1], E.R. Leite [1]

[1] CMDMC - LIEC/DQ/UFSCar - Via Washington Luiz, Km 235 - Caixa Postal 676; CEP 13.565-905 São Carlos - SP – Brazil – albarici@yahoo.com.br ;
[2] CMDMC - LIEC/IQ/UNESP-ARARAQUARA

Pigments are defined as organic or inorganic, particulate solid materials, which may be white, black, coloured or fluorescent, and are insoluble and chemically and physically inert in relation to the substrates onto which they are applied. In general, the structures of inorganic pigments display a high crystallinity, and contain oxides that serve as matrices to accommodate chromophores. Pigment colour will depend on its capacity to absorb the light in the spectrum in certain wavelengths in the visible region. Pigments are materials of great industrial importance, due to their wide range of application in building materials, glazes, paints, plastics and ceramics.

Recent years have witnessed a great preoccupation owing to environmental requirements that forbid the use of materials that impact the environment; for this reasons the use of metals such as lead and cadmium is avoided, due to their high toxicity, making it necessary to seek new non-toxic pigments. There is thus a great interest in obtaining red and orange coloured pigments, which are stable at high temperatures, and meet environmental regulations. However, great difficulties are encountered in producing these.

The pigments were synthesized by the polymer precursor method, which consists of the polyesterification reaction of the chelates, formed between a carboxyl acid and the metallic cations of interest with a polyalcohol, leading to the formation of a polymer resin. Calcination of this resin yielded the desired oxide. The samples were calcined at three different temperatures for one hour: 800, 900 and 1000°C, using a heating rate of 10°C per minute. Powders with doped zirconia pigments were synthesized with 5 mol% iron (ZF5) and 10 mol% iron (ZF10).

Figure 1 depicts the diffractograms of sample ZF5 and ZF10 powders. The results show the evolution of the phases with the variation in calcination temperature, indicating that at 800°C both formulations stabilized in the cubic crystalline form. At 900°C zirconia formation is observed in tetragonal form, as the major phase, and in the monoclinic form, as the minor phase, with traces of hematite (Fe_2O_3). The heat treatment at 1000°C causes almost complete conversion to the monoclinic form (baddeleyite): this is due to the growth of grain above the critical size for transformation. It was observed that Fe_2O_3 solubilized in zirconia at 800°C; however, at 900 and 1000°C, dissolution was partial. This is because the rise in calcination temperature reduces Fe_2O_3 solubility in the zirconia structure, in accordance with the equilibrium diagram of the system ZrO_2-Fe_2O_3.

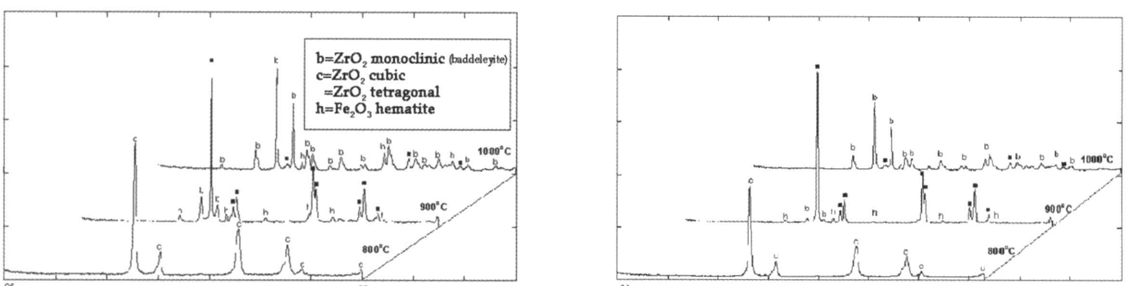

Figure 1. X-ray diffractograms of zirconia pigments (a) with 5 mol% iron (b) with 10 mol% iron after calcination at different temperatures.

Figure 2 displays the UV-visible spectrum for the ZF5 and ZF10 series. The results indicate that all the samples exhibited the typical spectral distribution of red coloured pigments, centred in the range from 605 to 750 nm. The sequence of spectra shows that the increase in calcination temperature, as well as the amount of dopant, reduces reflectance, indicating pigment darkening due to the reduction of iron oxide from state +3 to +2.

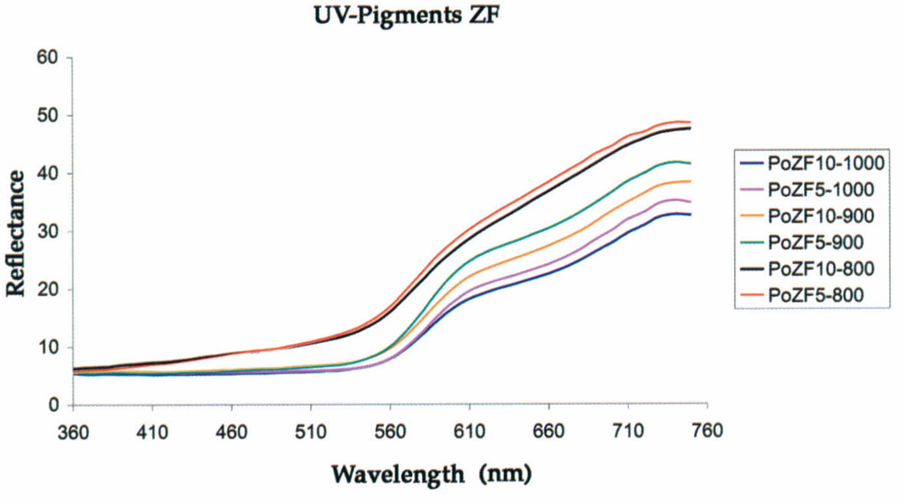

Figure 2. Reflectance spectra of the pigments obtained after calcination at 900, 1000 and 1100°C.

Table I details the colorimetric coordinates of the studied pigments, expressed in the CIELab system. These results confirm what was stated in the case of the evolution of the reflectance spectra in the UV-visible region, i.e., parameter L indicates that lightness is greater when calcination temperature is lower and the dopant amount smaller. The positive values of a* indicate the predominance of the red colour in all the samples obtained.

REFERENCE	T°C	L*	a*	b*
ZF5	800	49,247	18,726	25,180
	900	41,585	23,895	22,251
	1000	37,700	21,333	16,454
ZF10	800	48,328	18,296	23,026
	900	40,320	21,219	19,480
	1000	37,031	19,956	16,245

Table 1. CIELab colorimetric coordinates.

The specific surface area of the different samples was determined by means of the N_2 adsorption method (BET). Figure 3 plots the results obtained in the form of temperature versus surface area. The reduction of surface area with the increase in calcination temperature is due to the fact that particle growth is a thermally activated process.

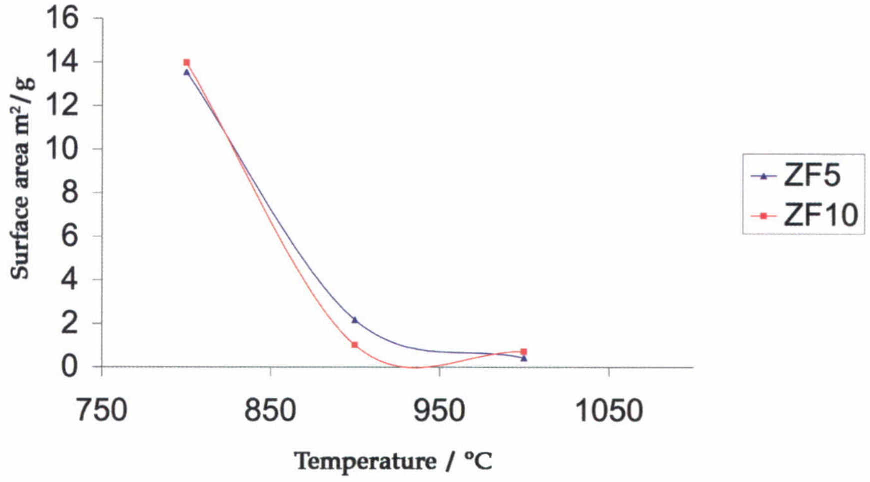

Figure 3. Plot of temperature as a function of surface area.

The Pechini process is appropriate for pigment synthesis in the ZrO_2-Fe_2O_3 system. The calcination temperature of 800°C was the most appropriate for extensive solubilization of iron oxide in the zirconia structure. The heat treatments above 800°C drastically reduced the total surface area of the resulting pigments. The spectroscopy results in the UV-visible region confirm that the samples obtained display the characteristic reflectance spectrum of commercial red pigments.