COBALT SILICATE-BASED CERAMIC COLOURS OBTAINED BY THE PECHINI METHOD

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Ceramic pigments are normally used in the ceramic industry to colour ceramic glazes. They are inorganic substances consisting of a ceramic matrix of a crystalline nature and a chromophore element (transition metal) that provides the colour. These substances have the following properties: thermal stability, insolubility in the glazes to which they are added, resistance to attack by chemical agents (acids and bases) and physical agents (abrasives), and should not produce gases in the glazes so as not to give rise to faults. Most of the oxides contained in such colours are crystals of mixed oxides, such as silicates, spinels and zircon oxides.

In this study, Co_2SiO_4 based ceramic colours were synthesised at a lower temperature (1000°C) compared to the oxide mixing method used in industry, in which the powders are normally calcined at 1200°C .

In the Pechini method, after dissolving the precursors in water, homogenisation takes place in ethylene glycol and citric acid with constant stirring in the 60-70°C range, to obtain a polymeric resin. This resin is subjected to heat treatment to produce a powder.

The basic idea of the method is to distribute the cations at an atomic level throughout the polymer structure. Calcination in oxidising atmosphere (400°C) then breaks up the polymer chain with subsequent carbon burnout.

The samples were characterised by scanning electron microscopy (SEM)), X-ray diffraction (XRD), infrared spectroscopy (IR), differential thermal analysis (DTA), thermogravimetry (TG) and reflectance spectroscopy.

DTA and TG analysis indicate that the exothermic range of 300-600°C is attributable to the oxidation of organic matter. The endothermic transformation peak around 900°C was associated with the transformation reaction

$$Co_3O_4 \Rightarrow 3CoO + 1/2\ O_2$$

Phase evolution in terms of heat-treatment temperature is illustrated in the diffractograms shown in Figure 1. It can be observed that only the spinel phase Co_3O_4 was found in the samples after heat treatment at 500°C . On raising the temperature to 900°C , the Co_2SiO_4 phase started to form, which agrees with the DTA and TG analysis data. After heat treatment, the sample was held at 1000°C for 14 hours, which yielded the single-phase system Co_2SiO_4. It should be pointed out, as shown in Figure 1, that the commercial colour sample obtained at 1200°C exhibited a second phase, silica, in the form of cristobalite.

The resulting colour was applied in a glossy ceramic frit. This was compared with the commercial colour applied under the same conditions.

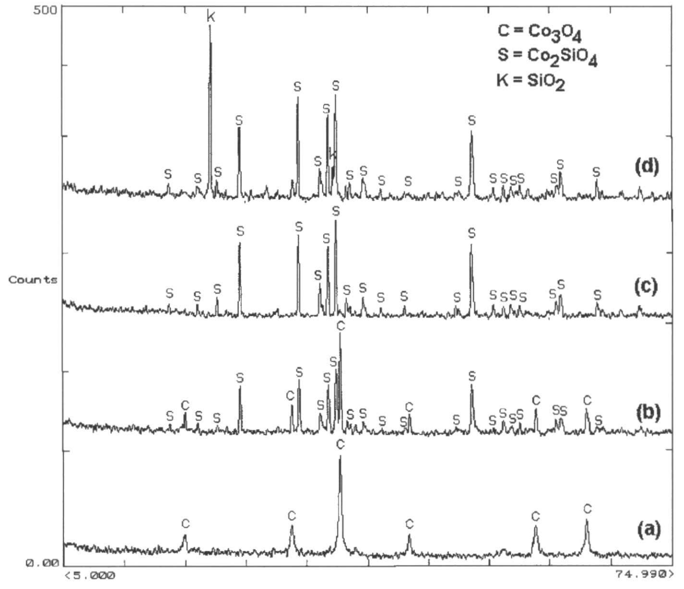

Figure 1. *X-ray diffractogram of the synthesised colour in its heat-treatment stages and of the commercial colour. (a) 500°C for 2 hours, (b) 900°C for 2 hours, (c) 1000°C for 14 hours, (d) commercial colour produced at 1200°C .*

IR analysis showed that the frequency band close to 660cm^{-1}, which is characteristic for the Co_3O_4 spinel became less intense after 900°C , while at the same time the frequency of the Co_2SiO_4 bands rose, which matches the XRD data in Figure 1.

SEM observation of the powder heat-treated at 1000°C revealed heterogeneous powder morphology.

The synthesised colour exhibited a very strong blue colour when compared with the commercial colour. Figure 2 shows that the synthesised colour exhibited higher reflectance values in the wavelengths of the purple and blue region in the range 360-490 nm than the commercial colour, indicating that the synthesised colour was purer and more homogeneous, which agrees with the XRD data.

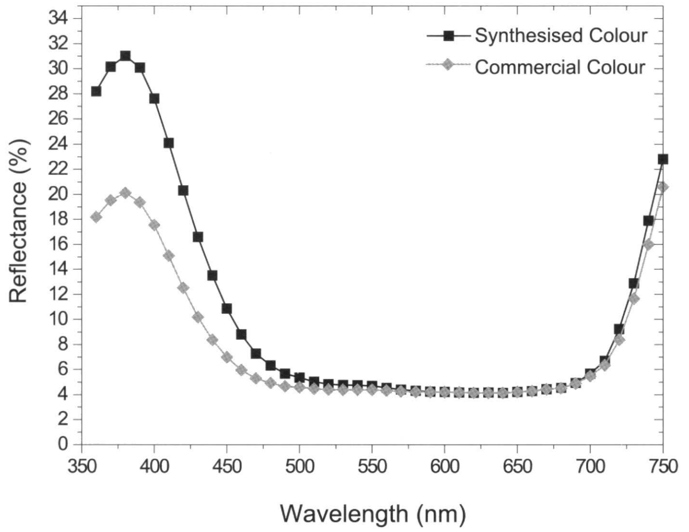

Figure 2. *Spectral curve of the synthesised colour and the commercial colour.*

The results allowed drawing the conclusion that the cobalt silicate-based colour made by the Pechini method exhibited an excellent quality colour.