Synthesis and characterization of lanthanum- and yttrium-doped Fe$_2$O$_3$ pigments

(Síntese e caracterização de pigmentos de Fe$_2$O$_3$ dopados com lantânio e ítrio)

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Abstract

Iron oxide has been doped with rare earth ions (yttrium or lanthanum) aiming at producing ceramic pigments with hues that vary from orange to brown. The powders were synthesized from polymeric precursors using the Pechini method and subsequently calcined between 900 and 1100 °C. The resulting pigments were characterized by BET, X-ray diffraction, colorimetric analysis, UV-visible, infrared (FTIR), particle size distribution and thermal analysis. The color depicted by La/Fe powders changed as the calcination temperature increased from 900 °C to 1100 °C, as established by the corresponding changes in the values of the colorimetric coordinates from L*$*$ a*$*$ b*$*$ = 49.003, 10.541, 12.609 to L*$*$ a*$*$ b*$*$ = 31.279, 6.096, 6.877. On the other hand, Y/Fe powders were little affected by similar changes in the calcination temperature, revealing the effect of yttrium on the color stability of the powder. The values of the colorimetric coordinates in this case varied from L*$*$ a*$*$ b*$*$ = 45.230, 17.315, 28.750 to L*$*$ a*$*$ b*$*$ = 51.631, 15.726, 25.825. Structural changes were also noticed as a function of the size of the rare earth ion added to the structure. Upon calcination at 900 °C, lanthanum stabilized the ABO$_3$-type perovskite structure whereas the presence of yttrium resulted in a mixture of oxides.

Keywords: rare earths, ceramic pigments, colorimetry.

INTRODUCTION

Mixed oxides, particularly those of general formula ABO$_3$ (A and B are d and f transition metals), which crystallize in the perovskite structure have been studied for a range of new applications. These materials are usually stable at high temperatures and depict a series of interesting electric, magnetic, catalytic and optical properties [1, 2]. Inorganic pigments, traditionally obtained from naturally occurring minerals or by ceramic processing [3, 4], have been produced using different approaches such as combustion synthesis [5], polymeric precursor method [6] and precipitation [7]. Alternative synthesis routes have been tested aiming at improved powder characteristics, especially particle size, which enhances the coloring effect of the pigment as it is used in ceramic glazes [8]. In general, light scattering improves with reduced particle size, producing glazes with superior optical performance [9]. In this context, ceramic pigments based on iron oxide (Fe$_2$O$_3$) doped with lanthanum or yttrium, were synthesized from polymeric precursors using Pechini’s method. The resulting powders were characterized and the effect of rare earth addition on the final color of the pigment was studied by UV-visible and colorimetric analyses.

EXPERIMENTAL PROCEDURE

RE-FeO$_3$ (RE = Y, Fe) mixed oxides were synthesized from polymeric precursors using the method proposed by Pechini [10]. Lanthanum nitrate La(NO$_3$)$_3$.6H$_2$O and Yttrium nitrate Y(NO$_3$)$_3$.6H$_2$O were obtained from the reaction of La$_2$O$_3$ or Y$_2$O$_3$ with citric acid (HNO$_3$), Aldrich Steinhein,
Germany). The concentrations of metallic ions La$^{3+}$ and Y$^{3+}$ were established by complexometric titration using EDTA. Fe$^{3+}$ citrate solution was prepared at 60 °C under constant stirring from Fe(Cl$_3$)$_3$aq., setting the molar ratio to 1:3 with respect to citric acid. La(NO$_3$)$_3$aq. or Y(NO$_3$)$_3$aq. were then mixed to the Fe$^{3+}$ citrate solution and heated up to 90 °C. Subsequently, ethyleneglycol was added at a ratio of 60:40 (citric acid to ethyleneglycol). This solution was stirred and heated up to the point where a transparent gel was formed. The gel was then calcined at 300 °C for 2 h at a heating rate of 5 °C/min. A sponge-like powder was formed and comminuted in a Pulverisette 2000 planetary mill.

The calcination temperature of the pigments was established by thermogravimetric analyses carried out under air in a Perkin Elmer system. The heating rate was 10 °C/min. Infrared patterns were used to evaluate whether organic residues remained in the material after calcination at 500, 700 or 900 °C. A Perkin Elmer FTIR-16 PC set-up was used to that end. KBr samples (1 wt.% pigment) were previously dried at 100 °C for 4 h and pressed under 4 ton during 5 min. The presence of crystalline phases was established by X-ray diffraction using a Shimadzu XRD-6000 diffractometer. The angular range 5° ≤ 2θ ≤ 100° was scanned using CuK$_\alpha$ radiation (λ = 1.5418 Å). The specific surface area of the pigments was estimated by BET N$_2$ adsorption in a Quantachrome NOVA 2000 system. For these analyses, 0.3 g powder samples were prepared at 300 °C under vacuum. Particle size distributions were obtained using a CILAS 1064 particle size analyzer. The morphology of the powders (previously coated with an Au film) was observed by scanning electron microscopy using a Philips XL 30 ESEM system. The diffuse reflectance of calcined powders was measured in the 300 to 800 nm range using a Gretac Macbeth 2180-2180 UV spectrophotometer using D65 lighting.

Finally, the color of the pigment was established from L*a*b* colorimetric coordinates according to CIE standards using

$$\Delta E^2 = L^2 + a^2 + b^2$$

(A)

where L* varies from black (0) to white (100), a* from green (-) to red (+), and b* from blue (-) to yellow (+).

**RESULTS**

The stages of thermal decomposition of the polymeric precursor to form RE-Fe$_2$O$_3$, (RE: La or Y) can be visualized in Figs. 1 and 2. The onset of decomposition took place at 50 °C with the decomposition of the citric acid present in the polymeric solution. Water decomposed up to 150 °C and organic material between 150 and 650 °C.

Absorption infrared spectra of the precursor powders (Fig. 3) revealed the presence of wide bands between 1500 and 1750 cm$^{-1}$ corresponding to the stretching of carboxylate groups (COO$^-$) of the organic material. Wide rounded bands corresponding to the stretching of (O-H) bonds, present in citric acid, and coordinated water were also observed at 3275 cm$^{-1}$. At 900°, the stretching of carboxylate groups (COO$^-$) were no longer observed. Instead, a band at 550 cm$^{-1}$ was
formed and could be attributed to oxide phases (Fig. 4).

X-ray diffraction patterns of samples calcined at 900 °C (Fig. 5) suggested the formation of LaFeO$_3$ depicting the perovskite structure and a polyphasic material consisting of Y$_2$O$_3$ and Fe$_2$O$_3$ (Fig. 6). Although the properties of lanthanum and yttrium are similar, their atomic radii are different, which affected the mechanisms that determine their occupancy in the host lattice. As a result, the corresponding powders were characterized by different colors determined

<table>
<thead>
<tr>
<th>Sample</th>
<th>Powder Pigments</th>
<th>ΔE</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaFe$^a$(900)</td>
<td></td>
<td>51.685</td>
<td>49.003</td>
<td>10.541</td>
<td>12.609</td>
</tr>
<tr>
<td>LaFe$^b$(1100)</td>
<td></td>
<td>32.601</td>
<td>31.279</td>
<td>6.096</td>
<td>6.877</td>
</tr>
<tr>
<td>YFe$^a$(900)</td>
<td></td>
<td>56.321</td>
<td>45.230</td>
<td>17.315</td>
<td>28.750</td>
</tr>
<tr>
<td>YFe$^b$(1100)</td>
<td></td>
<td>59.833</td>
<td>51.631</td>
<td>15.726</td>
<td>25.825</td>
</tr>
</tbody>
</table>

*T - Rare Earth (La, Y)

Table II - Effect of temperature on the surface area of pigments calcined at 900 °C and 1100 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>TR:Fe (ratio)</th>
<th>S$_{BET}$ (m$^2$g$^{-1}$)</th>
<th>Average Diameter (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaFe$^a$(900)</td>
<td>1:1</td>
<td>5.10</td>
<td>16.57</td>
</tr>
<tr>
<td>LaFe$^b$(1100)</td>
<td>1:1</td>
<td>3.20</td>
<td>19.25</td>
</tr>
<tr>
<td>YFe$^a$(900)</td>
<td>1:1</td>
<td>4.15</td>
<td>25.20</td>
</tr>
<tr>
<td>YFe$^b$(1100)</td>
<td>1:1</td>
<td>2.20</td>
<td>28.08</td>
</tr>
</tbody>
</table>

*T - samples annealed at 900 °C - t - samples annealed at 1100 °C

Table I - Colorimetric coordinates of calcined powders.
by the homogeneity of phase distribution.

UV-visible plots of La-Fe$_2$O$_3$ and Y-Fe$_2$O$_3$ (Fig. 7) included a band between 600 and 700 nm, characteristic of the emission of iron compounds. The colorimetric coordinates of the pigments were calculated (Table I). The positive values of a* indicated the reddish hue of both pigment systems. However, the La-Fe$_2$O$_3$ powder was darker, as suggested by smaller values of L*(49,003) to (31,279).

BET and particle size analyses (Table II) indicated that the specific surface area decreased and the average particle size increased as the calcination temperature increased from 900 ºC to 1100 ºC for both RE-Fe$_2$O$_3$ systems. The increase in particle size resulting from the increase in calcination temperature contributed to particle agglomeration as it could be seen from the SEM images of LaFeO$_3$ (Figs 8A and B) and Y$_2$O$_3$-Fe$_2$O$_3$ powders (Figs. 8C and D).

**CONCLUSIONS**

The addition of La$^{3+}$ or Y$^{3+}$ to Fe$_2$O$_3$ resulted in pigments of different colors. The La/Fe$_2$O$_3$ system depicted the perovskite structure whereas the addition of yttrium resulted in a polyphasic material consisting of Y$_2$O$_3$ and Fe$_2$O$_3$. The color of La/Fe powders changed with the calcination temperature whereas Y/Fe powders were little affected. SEM analyses revealed that both powders consisted of agglomeration of particles.

**REFERENCES**

(Rec. 01/08/2006, Ac. 22/09/2006)