SYNTHESIS OF HETEROMORPHIC IRON OXIDE RED PIGMENT FOR CERAMIC APPLICATIONS

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ABSTRACT

The use of natural inorganic pigments in the ceramic industry is steadily increasing. Natural inorganic pigments have low costs, compared with synthetic pigments. Iron oxide is a widely used natural pigment since it presents an ample variety of colours, is non-toxic and has a low cost. The red pigment has been a problem for the ceramic industry because the only one that is considered blood red does not work at temperatures higher than 1100 °C. Moreover, it is also toxic. Hematite is a natural iron ore, with a stable red colour up to 1000 °C. However the Fe^{+3} *ion is very reactive with ceramic glaze compositions, frits and ceramic bodies. In this context, the present work was undertaken with a view to investigating the synthesis processes of hematite particle occlusion in an amorphous silica matrix. Thus, goethite with average particle size between 4 and 2 mm was wet mixed with amorphous silica (surface area of 400* m^2/g*) in a ball mill for 5h. After homogenization the samples were dried in a laboratory furnace at 110°C, deaggregated and subsequently heat-treated in an electric furnace in the 1050-1200°C temperature range for 240 min. Finally, the heat-treated samples were analyzed by XRD and the pigment colours were determined by a UV-Vis spectrophotometer. The results indicate that pigment colour is influenced by the particle size of the iron oxide precursor, relative amounts of the oxide precursor and encapsulating matrix, as well as heat-treatment temperature and time (calcination).*

EXPERIMENTAL PROCEDURE

Natural goethite (having mean particle size in the range 2-4 mm) and amorphous silica (having a surface area of 400 m^2/g) were used as raw materials. Table 1 shows the raw materials proportions used for the preparation of each sample. The samples were wet mixed with acetone in a ball mill for 5 h so that very homogeneous slurries were obtained. The slurries were subsequently dried at 110°C to constant weight and deaggregated for calcination heat-treatments. Heat-treatments were carried out in an electric laboratory furnace in the 1050-1200°C temperature range for different times (60, 120, 240 and 360 minutes) in air by applying a heating rate of 20°C/min. The samples were then cooled down to room temperature. The heat-treated samples were subsequently subjected to XRD (Philips Xpert, year 1994) and UV-Vis spectrophotometer (Hunter Lab Color Quest) analyses for the determination of the mineralogical phases and calorimetric parameters. To determine the silica sintering temperature, a powdered sample was pressed in a laboratory press at 40 MPa. The thermal shrinkage curve was then determined in a dilatometer in air by applying a heating rate of 20°C/min.

Sample reference	Goethite (wt%)	Silica (wt%)
A90	10	90
A80	20	80
A70	30	70
A60	40	60
A50	50	50

Table 1: Weight Proportion of goethite and amorphous silica.

RESULTS

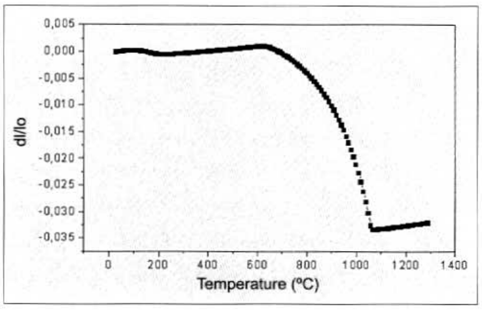

Figure 1: Linear thermal shrinkage curve of the amorphous silica.

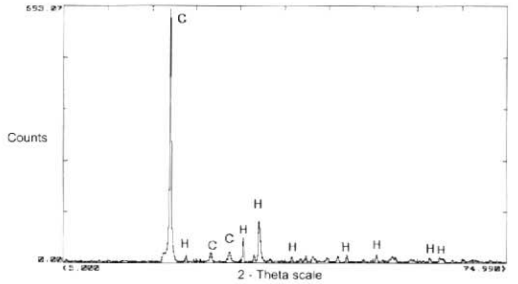

Figure 2: XRD patterns of sample A904 heat-treated at 1200 °C for 240 min. (C- Cristobalite, H- Hematite).

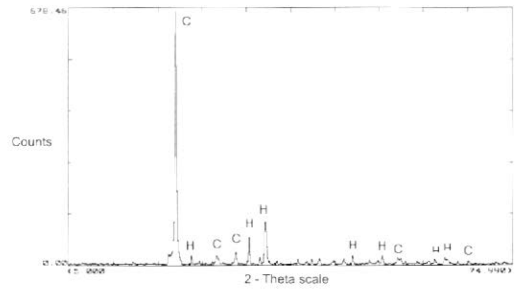

Figure 3: XRD patterns of sample A902 heat-treated at 1200 °C for 240 min. (C-Cristobalite, H-Hematite).

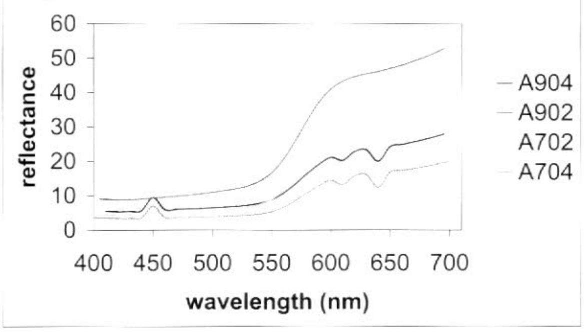

Figure 4: Reflectance spectra of iron oxide pigments.

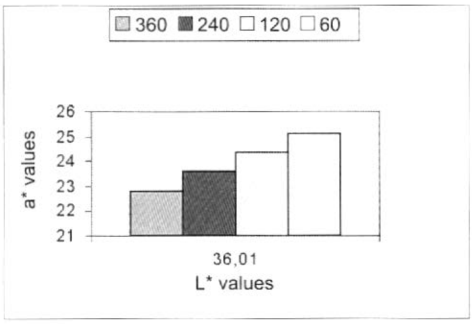

Figure 5: Evaluation of L and a* system for the iron oxide precursor with different heat-treatment temperature times, L*(luminosity), a*(red colour) (60-360 min.).*

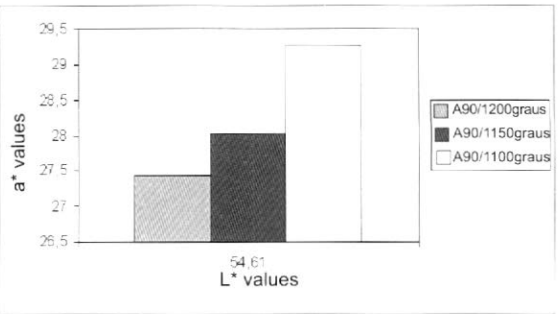

Figure 6: Evaluation of L and a* system for the iron oxide precursor with different heat-treatment temperatures, L*(luminosity), a*(red colour).*

DISCUSSION AND CONCLUSION

From the figures it can be seen that the same mineralogical or crystalline phases are involved (C- Cristobalite and H-Hematite) for all the samples. However, XRD intensity depends on particle size and crystal concentration. On the other hand, colour intensity do not show the same behaviour i.e., better results were obtained for lower iron oxide contents (10 wt%) and lower particle sizes (2 mm); the figures show the L* and a* parameters, and reflectance spectra, respectively. Although sample A70 shows higher iron oxide contents, lower colour intensity (red colour) is found than in sample A90. This result was also confirmed for samples with different iron oxide contents as Figure 4 shows, which indicates that there is an optimal proportion between the iron oxide and silica to obtain good occlusion and consequently good colour intensity. This behaviour can be explained by the fact that in this case, the silica present is not enough to protect every iron particle and consequently some of these iron particles become exposed to air yielding magnetite (Fe_3O_4 which has a black colour) according to the following reaction: $3Fe_2O_3$ (s) $\Leftrightarrow$ $2Fe_3O_4$ (s) ± O_2 (g). In fact according to LLUSAR, the occlusion mechanism in encapsulated pigments is directly related with the sintering and / or crystallization process of the matrix i.e., it must be adjusted to synchronize with the growth process of the occluded chromophore phase. Further investigations considering the temperature-time effects show that when heat-treatment temperature and time increase, the colour intensity of the obtained pigments decreases as Figures 5 and 6 show. These results agree with the mechanism proposed by LLUSAR, since crystal growth is expected when temperature and time increase, while colour intensity should decreases since the light path in this case is greater, which means lower reflectance.