PREPARATION OF THE NANOMETRIC SPINEL $Li_2CoTi_3O_8$ OBTAINED AT LOW TEMPERATURE FOR APPLICATION AS PIGMENT

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ABSTRACT

The objective of this study has been the preparation of a powder of the spinel phase $Li_2CoTi_3O_8$ with nanometric particle size by the polymer precursor method (Pechini). The desired nanometric $Li_2CoTi_3O_8$ spinel phase was obtained starting from 500°C. The spinel phase displayed a green colour at temperatures in the range between 400°C and 500°C, and a blue colour at temperatures between 600°C and 1000°C.

1. INTRODUCTION

According to the DCMA (Dry Colors Manufacturers Association) classification, the materials that crystallize with the $A[B]_2O_4$ type of spinel structure are currently the most widely used pigments because they provide a very large variety of shades. On the other hand, oxides with a spinel type structure also have important uses in view of their catalytic, electric and magnetic characteristics. The spinel has the general formula AB_2O_4, where A are the cations in tetrahedral sites and B are the cations in octahedral sites of the cubic structure with group of symmetry Fd3m. These crystalline structures can accommodate a great variety of cations, an effect that is characteristic of the spinel. Two crystallographic forms are possible in the spinel. The spinel with AB_2O_4 distribution and the inverse form with $B(AB)O_4$ distribution. In both cases, the parenthesis represents the octahedral position. Another distribution is also possible, with an intermediate type of representation having the formula $(A_{i-1}B_i)[A_iB_{2-i}]O_4$. The polymer precursor method, known as the Pechini method, which was the method used in this study, is based on the formation of a chelate between the cations that are mixed with a hydrocarboxylic acid like citric acid.

In view of the above, the objectives of this work have been: preparation of the $Li_2CoTi_3O_8$ phase with nanometric particles and verification of the pigments obtained for their possible use as pigments.

2. EXPERIMENTAL PROCEDURE

The resin for the $Li_2CoTi_3O_8$ spinel phase was synthesized by the polymer precursor method developed by Pechini, in the following way. First, citric acid in aqueous medium was added in a proportion of 3 moles in relation to the sum of the cations involved in the synthesis with temperatures up to 70°C. After complete dissolution, this was added to a titanium citrate solution, which was at the same temperature. Next glycol ethylene was added in a proportion of 40/60 (% by mass) in relation to the citric acid. After solubilization, the temperature was gradually raised to 100°C to promote esterification, thus forming the polymer resin. After the resin had been prepared, this was subjected to a preliminary calcination at a temperature of 300°C for 1 hour, followed by disaggregation in an agate mortar. After disaggregation of the material, the powder was heat treated at temperatures that ranged from 400°C to 1000°C, at a heating rate of 10°C/min in ambient atmosphere for 4 hours.

3. RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction of the pigment calcined at temperatures of 400°C to 1000°C, with a soak of 4 hours, and intervals of 100°C. The diffractograms display no intermediate phases. This indicates that the sample calcined at 400°C is still in an amorphous state and that the crystallization process begins at 500°C. On the other hand, the increase in calcination temperature leads to a gradual growth of crystallite size. The data show that the phase has the following stoichiometry $Li_{0.55}Co_{0.45}[(Li_{0.45}Co_{0.05})Ti_{1.5}]O_4$. $Li_{0.55}Co_{0.45}$ in tetrahedral positions and $Li_{0.45}Co_{0.05}Ti_{1.5}$ in octahedral positions of the group of symmetry $P4_332$.

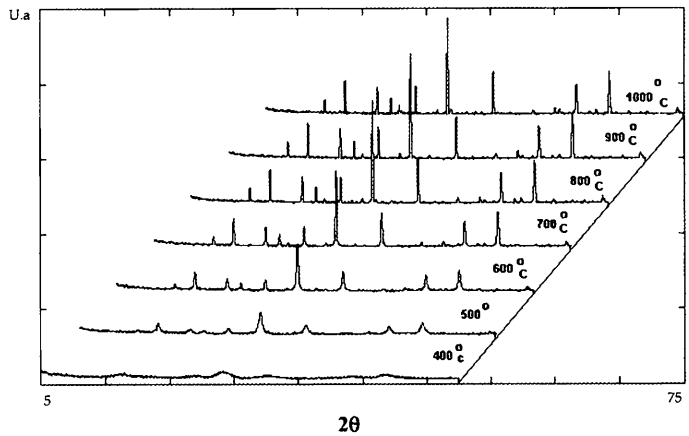

Figure 1

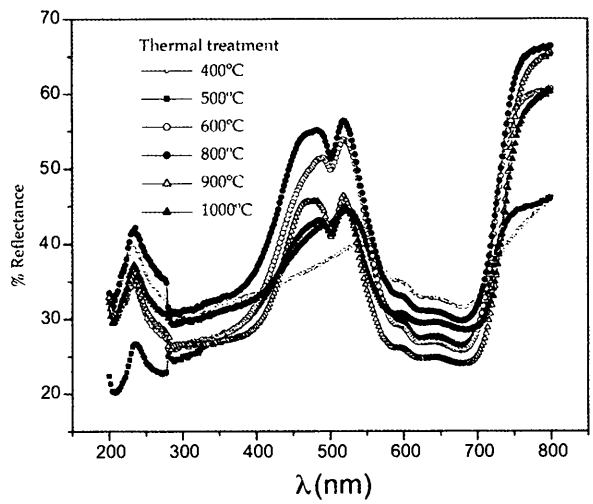

Figure 2

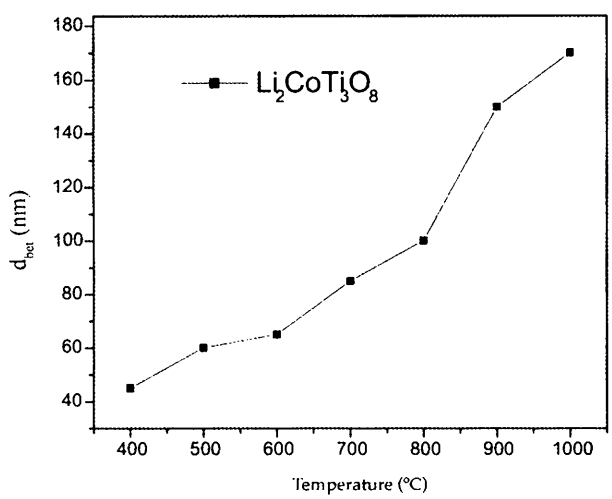

Figure 3

Figure 2 depicts the UV-Vis curves, with reflectance versus wavelength (nm) of the $Li_2CoTi_3O_8$ phase for temperatures from 400°C to 1000°C. It can be observed that at temperatures of 400°C and 500°C, the pigments display a green coloration, confirmed by the characteristic band in the 510 and 530nm region. For the powders treated at temperatures between 600°C and 1000°C, the pigments display a blue

coloration, confirmed by the characteristic bands in the 500nm region. The pigment calcined at 400°C exhibits an amorphous structure. The pigment calcined at 500°C shows the commencement of the characteristic band of the colour between green and blue. According to the refinement data with the Rietveld method, this phase exhibits the following cation distribution, $Li_{0.55}$ $Co_{0.45}$ $[(Li_{0.45}$ $Co_{0.05})Ti_{1.5}]O_4$. The UV-Visible data were correlated with the Rietveld refinement; it is observed that the pigments calcined at these two temperatures (400°C and 500°C), on not having a defined structure, can have a cobalt deficiency in the octahedral positions. Analysis of the powders after calcination between 600°C and 1000°C shows a band around 500nm, indicating that the colour of the pigment is already defined. It is furthermore observed that with the increase in calcination temperature, the reflection diminishes; this is due to the homogeneity of the Pechini method.

Figure 3 plots temperature against particle diameter by the BET method. It shows that raising temperature increases particle size. Up to 800°C, the pigment has a nanometric size. Figure 4 shows the colorimetric measurements (CIELab). Starting from 600°C, where we already verified that the phase was in a crystalline form, a change of symmetry is evidenced, which was discussed above; therefore, it is at this temperature when the coloration changes. The value of L* decreases linearly from 600°C with increasing temperature. This is due to the growth of particle size observed previously in Figure 3. We also observed this in the a* and b* coordinates; at temperatures between 700°C and 900°C the intensity of this colour is maintained. Figure 4.

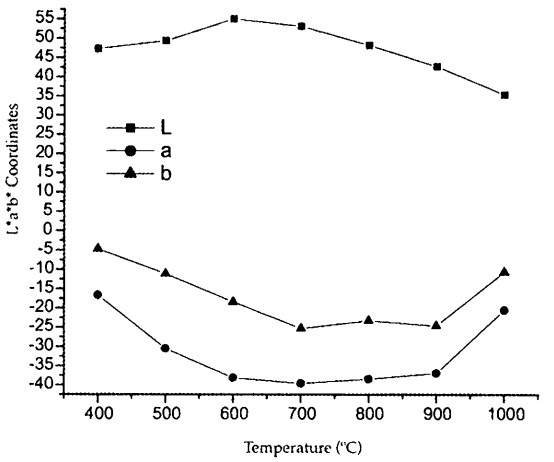

Figure 4

4. CONCLUSIONS

The Pechini method allows obtaining the $Li_2CoTi_3O_8$ spinel phase starting at 500°C on a nanometric scale. The spinel phase displays a green colour at low temperatures between 400°C and 500°C and a blue colour at temperatures between 600°C and 1000°C. Therefore, the results demonstrate the feasibility of using this pigment with the $Li_2CoTi_3O_8$ phase, since these pigments exhibit a stable coloration at low calcination temperatures and have a nanometric scale.

5. ACKNOWLEDGEMENTS

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