

Synthesis of Ceramic Pigments ACr_2O_4 Using the Non-Conventional Method of Co-Precipitation Assisted by Ultrasound and High Energy Milling

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Received 18 July 2014; revised 19 August 2014; accepted 18 September 2014

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Abstract

In this research ceramic pigments have been synthesized with crystalline spinel structure and chromium based with a stoichiometry ACr_2O_4 . A was an element with +2 valence metal, in this case, metals were zinc and iron, these pigments have been synthesized by non-conventional methods like the co-precipitation assisted by ultrasound and high milling energy. Pigments were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), spectrophotometry, and colorimetric CIELab method. Results showed that it was possible to obtain a crystalline desired structure at temperatures below 900°C by non-conventional methods. These results showed the advantages of ceramic pigments obtained by alternative routes, because it was possible to have a better control over stoichiometry and colorimetric structure properties. Furthermore, they were obtained at temperatures lower than those used by the traditional ceramic route.

Keywords

Pigments, Synthesis, Ceramics, Chemical Reactions, Color

1. Introduction

Ceramic pigments have been used in the ceramic industry to decorate plates, tiles, floors, and walls, for this reason they are very important in the construction industry. Ceramic pigments are inorganic chemical compounds, which provide color and are insoluble in a medium with which they do not interact physically or chemically [1].

How to cite this paper: Jaramillo Nieves, L.J., Restrepo Baena, O.J. and Tobón, J.I. (2014) Synthesis of Ceramic Pigments ACr_2O_4 Using the Non-Conventional Method of Co-Precipitation Assisted by Ultrasound and High Energy Milling. *Open Journal of Inorganic Non-Metallic Materials*, 4, 54-63. <http://dx.doi.org/10.4236/ojinm.2014.44008>

Ceramic pigments have different crystal structures, such as the spinel structure. Spinel type structures feature high strength, high thermal stability, low sintering temperature and easy incorporation of chromophore ions in the lattice, obtaining different colored pigments [2]-[8].

Traditionally, the synthesis of ceramic pigments has been led by the conventional ceramic way, but in recent years there has been a rise in the implementation of non-conventional methods. One reason for this is the importance of decreasing the temperature and time of the heat treatment with the corresponding reduction in gas emissions. Most synthesis methods employed are mainly solid-state reaction [9], sol gel [10], microemulsion [5], co-precipitation [11] [12], hydrothermal [12] [13], and polymeric precursor method [14]-[17].

In this work, the methods employed were ultrasound-assisted co-precipitation and high-energy milling.

Co-precipitation is important to avoid many environmental problems related to water resources, concentrations of metals in aqueous systems and technology for wastewater treatment. Co-precipitation varies in each case and the partition in the solid phase can be accomplished by surface adsorption, ion exchange, precipitation of the surface, and formation of occlusion solid solution [18]. A modification of this method is the sonochemical way, which is the use of irradiation with ultrasonic waves [19].

Mechanochemical synthesis involves high energy milling of the reactants powders; in this case they are oxides. Its effect is to induce or directly activate the chemical reaction in a subsequent heat treatment at a relatively low temperature. Types of high-energy grinding are distinguished by the nature of the reagents and chemicals and the structural changes during the process [20] [21].

2. Experimental

For this synthesis of ceramic pigments, the structure is defined as ACr_2O_4 , where A is a metal with valence +2, for this case metals are Fe and Zn.

2.1. Co-Precipitation Method Assisted by Ultrasound

The raw materials used were: $FeCl_2 \cdot 4H_2O$ PANREAC, $ZnCl_2$ CARLOERBA, $CrCl_3 \cdot 6H_2O$ MERCK. Reagent grade were used. With these salts, aqueous solution was prepared using distilled water, at a temperature of 70°C. This solution was added drop wise to an aqueous solution containing NaOH MERCK (reagent grade), for pH adjustment, (pH was between 11 and 12), KNO_3 as an oxidizing agent, (reagent grade, MALLINKRODT), at the same conditions. This solution was placed in ultrasound equipment and left for one hour, then allowed to stand for a few minutes and was vacuum filtered. The precipitate was washed with water and ethanol to remove soluble salts and again was filtered. The product was dried in an electric stove at 100°C for 12 hours, and then the sample was subjected to a heat treatment for 8 hours at 700°C. The heating rate was 5°C per minute.

The number of MERCK raw materials were two; NaOH and $CrCl_3 \cdot 6H_2O$.

2.2. Method of High Energy Milling

The raw materials were industrial grade Fe_2O_3 , ZnO and Cr_2O_3 . These oxides were ground in a suspension with a ratio of 40% of solids. This suspension was added to the grinding vessel containing alumina balls and placed in a planetary mill. The rotational speed was 250 rpm during 2 hours. After that, the suspension was dried at 100°C for 24 hours, then, the powders were de-agglomerated and sieved by sieve #100. Finally, the sample was subjected to a heat treatment for 8 hours at 700°C. The heating rate was 5°C per minute.

2.3. Characterization of Samples

Crystalline phases were determined by X-ray diffraction (XRD) in a PANalytical diffractometer, model XPert-Pro, using $CuK\alpha$ radiation of 1.54060 Å, from 4° to 75°, at a rate of 0.02°/min and 400 cps, and analyzed with the software X'Pert Highscore Plus.

Morphology was observed with a scanning electron microscope (SEM), JEOL model 5410 by backscattered electrons and secondary electrons mode, BE and SE respectively.

The spectral reflectance and the colorimetric coordinates were measured in a spectrophotometer UV-VIS-NIR, Glacier TM X with a CCD linear array, ranging from 200 nm to 1025 nm, the illuminant was D65 CIE and ASTM E1349-06 [22]. The CIE standard was 1964, and the software used was BWspec 3.26.

Table 1 shows the nomenclature and the conditions of preparation of the pigments which were characterized.

The nomenclature indicates to each cases the elements; Zn (Z), Cr (C), and O (O). The number indicates to co-precipitation the number of testing or sample. For High milling energy the numbers indicates; the two first are the rpm of the milling, for this case was 250 (25) rpm, the third is the time of milling, the two last are the temperature 700°C (7) and time 8 h (8) thermal treatment respectively. These pigments were named with a design of experiments and the best pigments were selected to compare the methodologies.

3. Results and Discussion

3.1. Co-Precipitation Method Assisted by Ultrasound

In **Figure 1**, the peaks of the spinel structure are shown. The pigment showed just one peak of another phase, zinc oxide. But the sample is composed mainly of a spinel phase. The positions of the peaks correspond to zinc chromite, showing that the method, the time and the heat treatment temperature were adequate to obtain the pigment ZnCr_2O_4 .

Figure 2 shows the micrographs of pigment ZCO3. a) This picture was obtained at 10,000× magnification, SE mode. The particles shown permit their identification and show how the crystals grew. These particles do not

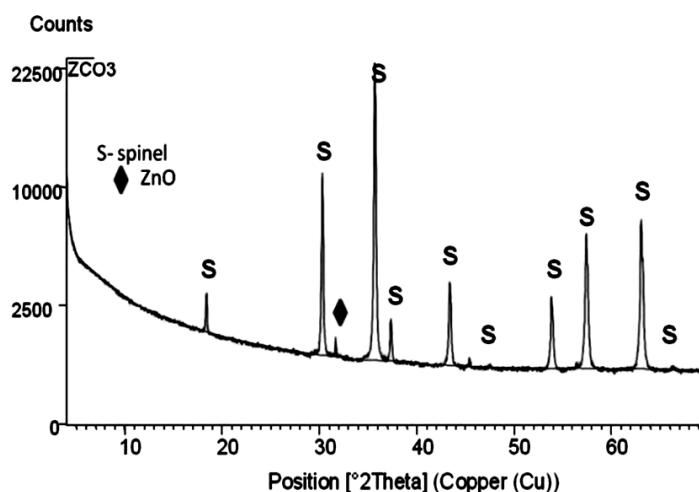


Figure 1. X-ray diffraction of ZCO3.

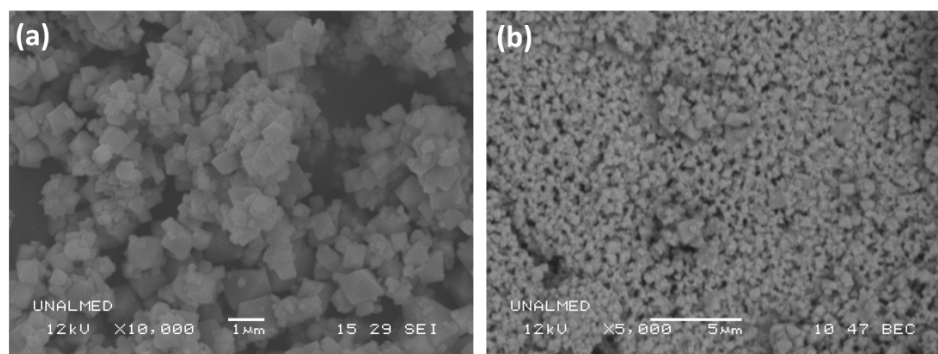


Figure 2. SEM image of ZCO3 (a) SE mode and (b) BE mode.

Table 1. Nomenclature and conditions of characterized pigments.

Sample	Coprec-Assist Ultrasound	High milling energy	Time
ZnCr_2O_4	ZCO3	ZCO25278	8 h/700°C
FeCr_2O_4	FCO3	FCO25278	8 h/700°C

exhibit big agglomerates but instead each particle can be easily distinguished, also one can observe a homogeneous particle size. b) This picture was obtained at 5000× magnification, the homogeneity of the sample can be seen, since the image taken was in BE mode, and the particles do not have differences in shades, this indicates the uniformity of the pigment's composition.

Figure 3 shows the reflectance spectrum of ZCO3. It can be seen that the pigment exhibits a maximum at approximately 510 nm, which corresponds to green. Also a maximum can be seen at 650 nm suggesting the presence of shades between yellow and orange. The reflectance factor is about 50%.

In **Table 2**, the colorimetric coordinates L^* a^* b^* of pigment ZCO3 is shown. The L^* coordinate is about 60, which indicates that a pigment tends to be clear. The a^* coordinate is negative which was expected, because that indicates the presence of green and the b^* coordinate is positive, thus showing yellow. This pigment has a gray-green hue.

Figure 4 shows the diffractogram for the FCO3 pigment. Peaks of the crystal structure are shown, the main phase is chromite iron spinel and does not have secondary phases, and the peaks are well defined, indicating that FCO3 is crystalline and that this method of synthesis produced correct results.

In **Figure 5** the micrograph of FCO3 at 10000× magnification is shown. We can see that the particles have a size below 1 μm and exhibit an elongated shape that is quite visible. This sample has small agglomerates of these particles.

In **Figure 6** the reflectance spectrum of pigment FCO3 is shown. It presents a small reflectance factor, less than 8%. This indicates that the sample is very dark, with peaks at 420, 480, 530, 560, and 700 nm, and red tones predominate.

In **Table 3** the colorimetric coordinates of the pigment FCO3 is shown. The L^* coordinate is low, this around

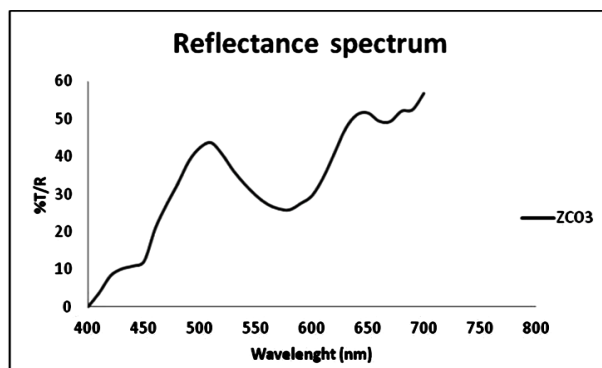


Figure 3. Reflectance spectrum of ZCO3.

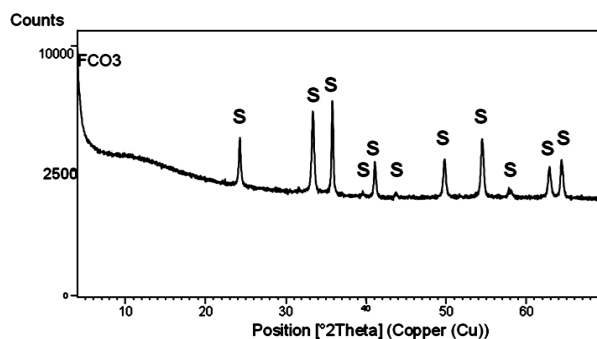


Figure 4. X-ray diffraction of FCO3.

Table 2. Colorimetric coordinates L^* a^* b^* ZCO3.

L^*	a^*	b^*
64.105	-9.087	22.866

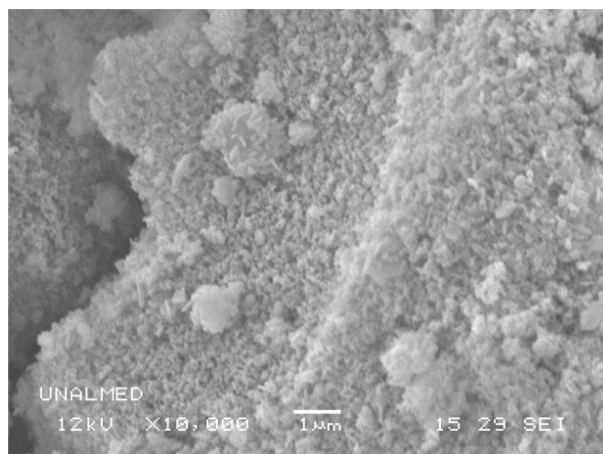


Figure 5. SEM image of FCO3.

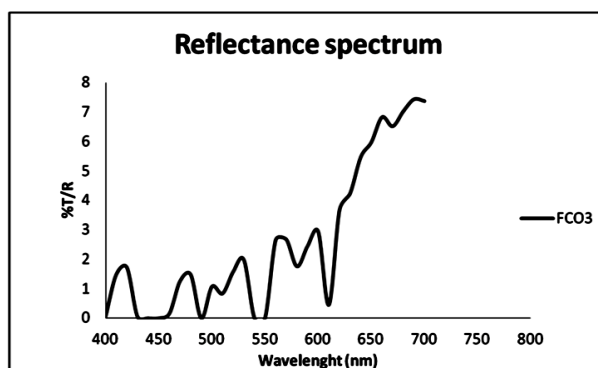


Figure 6. Reflectance spectrum of FCO3.

Table 3. Colorimetric coordinates L^* a^* b^* FCO3.

L^*	a^*	b^*
15.754	17.447	19.523

15 showing that the sample is dark, a^* and b^* are positive, corresponding to red and yellow respectively, yielding a brown-black color.

3.2. High Energymilling Method

In **Figure 7** the diffractogram of the ZCO25278 pigment (A is Zn) is shown. This sample presents spinel as the main phase, but also secondary phases like Al_2O_3 , Cr_2O_3 and ZnO. This is because the alumina balls produced wear in the long grinding experiments, which cause deterioration; therefore these phases are present because the time is not enough to ensure that all the raw materials react.

Figure 8(a) shows the SEM micrograph, SE mode, taken at 10000 \times magnification and in **Figure 8(b)** a 5000 \times magnification BE mode is shown, there the agglomerated particles are small, and the sample shows a good distribution and homogeneity, that is very clear in **Figure 8(b)**, because there is no variations in the particles' color.

In **Figure 9** the reflectance spectrum of the pigment is shown. It has a peak at 530 nm indicating the presence of a green hue and also has a less defined peak at 650 nm that corresponds to yellow. The reflectance is around 70%, showing that the pigment is clear.

In **Table 4** the colorimetric coordinates of the pigment ZCO25278 is shown, the L^* coordinate is around 80, therefore the pigment is clear and a^* is negative and thus is a grayish green and b^* is positive indicating the

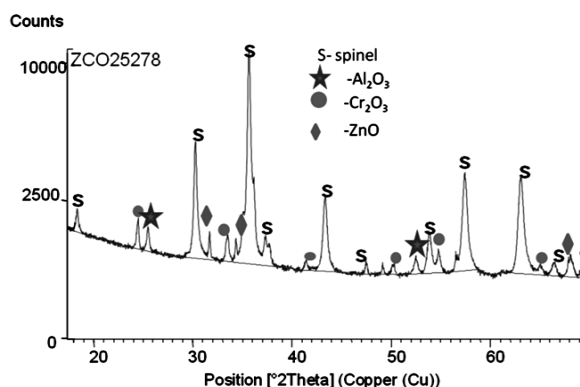


Figure 7. X-ray diffraction of ZCO25278.

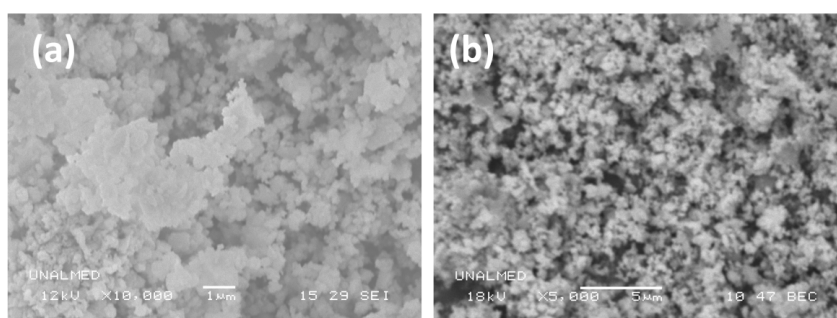


Figure 8. SEM image of ZCO25278 (a) SE mode (b) BE mode.

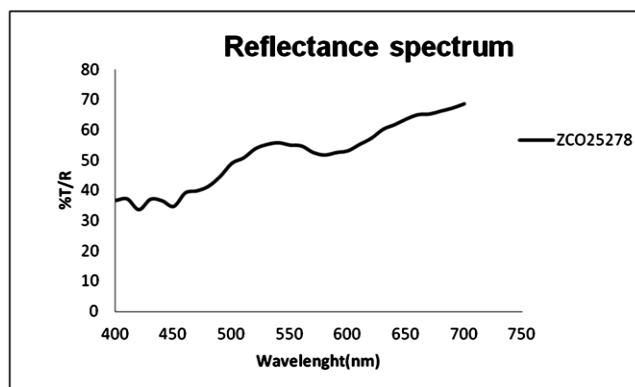


Figure 9. Reflectance spectrum of ZCO25278.

Table 4. Colorimetric coordinates L^* a^* b^* ZCO25278.

L^*	a^*	b^*
78.134	-3.683	16.632

presence of yellow.

In **Figure 10** the diffractogram of the FCO25278 pigment is shown (A is Fe). It can be observed, the diffractogram indicates the desired spinel phase, but also has secondary phases, of Fe_2O_3 and Cr_2O_3 . This shows that the energy supplied to the system is not sufficient to reach a complete conversion.

In **Figure 11** the SEM micrograph of pigment FCO25278 is shown, in SE mode. The image was taken at 10,000 \times magnification and it shows quite small agglomerates of small particles, less than 1 μm in size.

In **Figure 12** the micrograph of pigment FCO25278, BE mode, is shown, the homogeneity of the pigment can

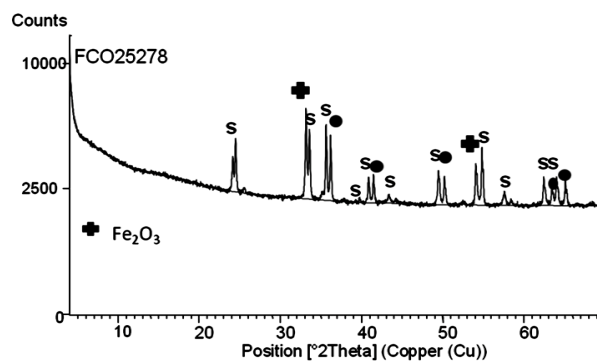


Figure 10. X-ray diffraction of FCO25278.

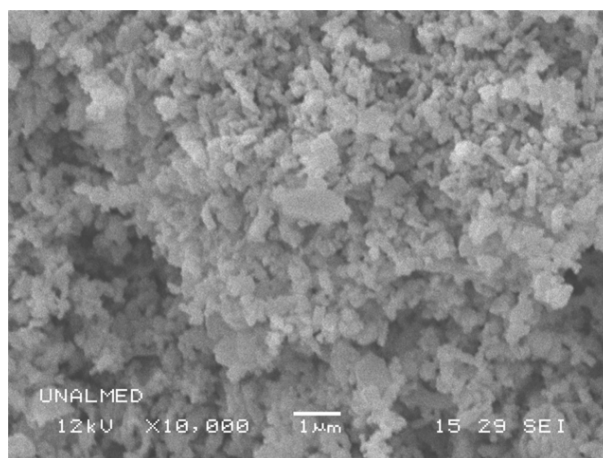


Figure 11. SEM image of FCO25278, SE mode.

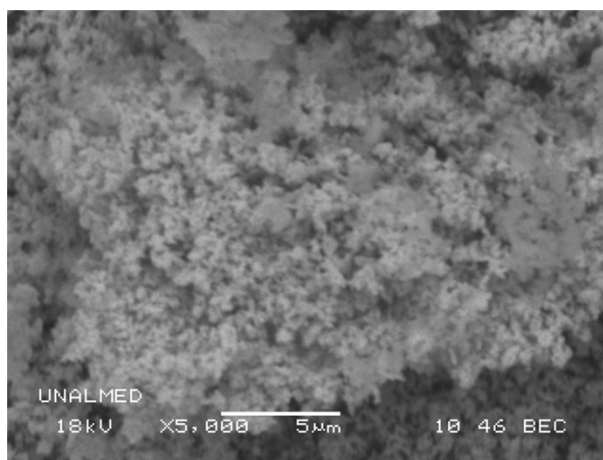


Figure 12. SEM image of FCO25278, BE mode.

be observed, because no differences are observed in the hues, the image was taken at 5000 \times magnification.

In **Figure 13** the reflectance spectrum of pigment FCO25278 is shown. The curve has an upward trend from 550 nm to 700 nm, indicating orange and red hues. The sample has a reflectance factor of approximately 40%, and therefore is a relatively dark sample.

In **Table 5** the colorimetric coordinates of the pigment FCO25278 is shown. The coordinates a^* and b^* are positive, showing that the pigment has a dark red hue.

In **Figure 14** the pigments obtained by the different methods of synthesis employed is shown.

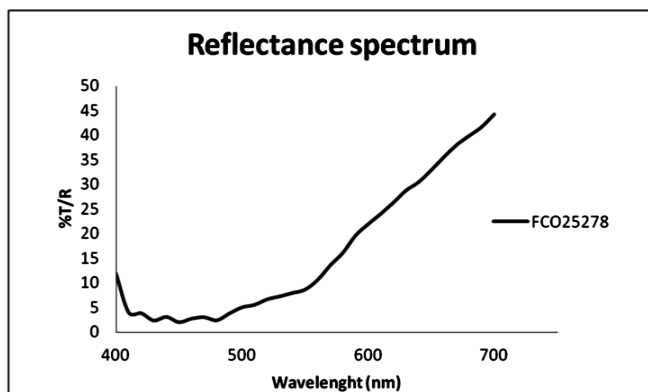


Figure 13. Reflectance spectrum of FCO25278.

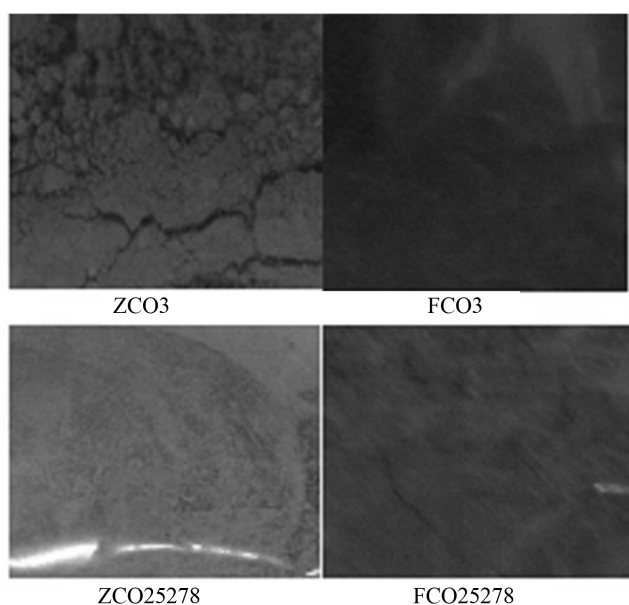


Figure 14. Tones of pigments obtained by different routes.

Table 5. Colorimetric coordinates L^* a^* b^* FCO25278.

L^*	a^*	b^*
42.405	24.219	38.282

The evaluation of the two unconventional synthesis routes was carried out; the method that yielded better results is based on ultrasound-assisted co-precipitation, because the expected color was achieved, in each case, green-gray for $ZnCr_2O_4$ and black-brown for $FeCr_2O_4$, the desired crystalline phases, spinels, a homogeneous particle size less than $1\ \mu m$, with the correct morphology and homogeneous chemical composition. The method of high energy milling also obtained a spinel phase and homogeneity of particle sizes, however, there was an incomplete reaction, since oxides were present in a secondary phase and also the hue in the case of $FeCr_2O_4$ was not as expected. This is because the co-precipitation method from salt solutions which contain scattered ions enables the more efficient thermal treatment of the reaction, while high energy milling needs to break the bonds of the oxides first which then split and form new links to the desired crystalline phase and quite possibly the applied energy has not been sufficient to achieve what was intended, although it was noted that the sizes are small which helps to increase the reactivity in the process, which may also be required for another body grinder to achieve greater energy to form the spinel phase.

4. Conclusions

According to the results presented, pigments obtained via ultrasound assisted co-precipitation and high-energy milling showed that very good properties were obtained, since all obtained the spinel crystal phase, the tones of pigments were within expectations with small deviations and homogeneity in particle size and the composition were good. The co-precipitation method assisted by ultrasound showed the best result in every way.

In the ultrasound assisted co-precipitation method, ceramic pigments were obtained with the desired stoichiometry and structure. Generally the pigments obtained by this method showed particle sizes of about 1 micron or less, good homogeneity in morphology and chemical composition. The reflectance factor and colorimetric coordinate's characteristics exhibited by the pigments were comparable to products obtained by traditional routes in the industry which are obtained at temperatures above 1000°C. Therefore this method achieved good quality pigments obtained at lower temperatures and in less time than the heat treatment in the conventional ceramic method.

Regarding the method of high-energy milling, although all samples exhibited spinel phase pigments, they also exhibited secondary phases of oxides. This may be because the energy applied, or the grinding time was not enough for all the materials to react as expected and this was evident in the color of FCO25278, because a darker tone was expected between brown and black, however, a dark red was observed. The results of the experiments also show that the reaction between iron and chromium required more energy for the ion migration compared to zinc and chromium. But the high-energy milling method cannot be ruled out, because good results may be achieved by optimizing some parameters, such as time of grinding, the mill speed, the ratio of solids and also the type of balls, and then a pigment with the right features for this type of structure may be obtained. Also the method could also be used for other systems where it could provide better pigmentation results.

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