# CERAMIC PIGMENT MICROWAVE PROCESSING

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## ABSTRACT

*The use of microwaves in solid-state processing is an alternative technique that has developed rapidly in recent years. A large range of different processes is presented, such as synthesis, powders preparation, joining, sintering, drying and others. Metallic oxides have been widely used as pigments in the preparation of enamels for ceramic coatings. The characteristics of the final product strongly depend on its physico-chemical and structural properties. This work shows the influence of microwave heating and hybrid heating of the oxide mixtures on the final properties of the pigments. The radicals (Cr-Fe-Zn) brown and (Cr-Fe-Co-Ni) black were prepared. The main goal is to understand the behaviour of the processed materials under microwave radiation.*

**KEYWORDS:** Microwave, Ceramic Pigments, Oxides.

## INTRODUCTION

The need of more improvement and versatility in all ceramic processing stages (from ceramic formulation to final product testing) lead the industries to invest in partnerships with Research Centers and Universities, mobilizing their technical staff in order to understand the phenomena related with manufacturing the product. It is important in ceramic enamel production that all batches have approximately the same tonality, among other physico-chemical characteristics[1]. However, the variation of raw-material properties and ceramic processing (milling equipment, milling performance, coating techniques, firing temperature), make these requirements difficult, but not impossible to accomplish[2, 3]. In the last few years, the demand for coloured products has led the ceramic industry to follow this tendency in the production of tile ware, sanitaryware, tableware and decoration products, with the aim to differentiate them. The necessity to understand how frits (major raw material in the enamel formulation) behave during firing has made research into its properties more developed in relation to other materials used to form ceramic products. Thus, it is important to understand very well the raw materials that traditionally contribute colour to ceramic enamels and the peculiarities observed during their processing[1].

**Ceramic Pigments:** An inorganic (ceramic) pigment is defined as a calcined material having one or more metallic oxides that, when added to an enamel, provide the ceramic product with a uniform colour by means of the formation of a coloured glass coating. Structurally, a network forms the glaze in which both chromophore elements and modifiers come together in order to stabilize or enhance reaffirm the effectiveness of the colorant. Brown and black pigments are almost always formed by spinel structures. The crystalline structure of the spinel group is very complex. Oxygen ions are packed densely, forming parallel planes in relation to the octahedral faces. Divalent cations ($Co^{2+}$, $Mg^{2+}$, $Fe^{2+}$) are bonded with four oxygen ions in a tetrahedral arrangement, while trivalent cations ($Al^{3+}$, $Fe^{3+}$, $Cr^{3+}$) are linked with six oxygen ions pertaining to the octahedral vertices of the structure. Each oxygen ion is linked with one divalent and with three trivalent cations. The final product, the enamel, is strongly influenced by both size distribution and stability of the raw material composing it. Thus, pigment particle size – micronized or not – will directly determine the type of chromatic effect after firing.

**Microwaves:** Material processing using microwaves has been investigated as an alternative to traditional calcination processes[4, 5]. In this kind of process the thermal energy is supplied directly to the material being processed due its interaction with the microwave field, resulting in uniform material heating if the best processing conditions are achieved, i.e., the complete interaction of the microwave field with the processed material. These conditions are determined by the study of the material dielectric properties[6, 7]. The principal advantages of this process include higher heating rates as well as higher productivity. The final properties (physico-mechanical) of materials processed with this technique could thus be improved, since temperature gradients between the surface and the centre of a specimen can be eliminated if the process is optimized[5, 8]. The increasing need for more economic and environmentally correct manufacturing methods has taken researchers of technological ceramics, as in the United States, Japan, France, England and Germany, and of traditional ceramics, as in Spain and Italy, to search for alternative techniques like microwave processing. The use of microwaves on a laboratory scale has been widespread for processing materials like polymers, wood, metals, ceramic and composites. The development of processes such as drying, sintering, welding and powder preparation has stimulated research in the application of microwave processing for ceramic materials and solid state Chemistry[4, 5].

## METHODOLOGY

**Sample preparation:** The pigments studied (Cr-Fe-Zn (brown) and Cr-Fe-Co-Ni (black) oxide systems) had been obtained from the production site of a commercial facility. Samples were prepared for each kind of pigment with the raw material only milled (0,8% mass residue in 325 mesh) and after micronization (0% mass residue in 325 mesh). The crude pigments were then calcined conventionally in an intermittent gas kiln according the following cycles: 1250°C during 16h for the brown pigment and 1280°C during 16h for the black one, obtaining batches of 400kg each. Microwave calcination was carried out using the methods of simple heating and hybrid heating (30% microwave). Both used 6g of crude pigment. In the simple heating method the samples were placed in a quartz tube and heated under microwaves using a guide wave reactor. In the hybrid heating method a dissipative ceramic involving the quartz tube was used. The temperature was measured using metallic armoured thermocouples in both situations. The heating cycle for the simple irradiation process was 150W during 2min for the black pigment and 150W during 3min for the brown pigment. The hybrid heating method used 200W during 4min for both pigments. The final temperature measured in all cycles was 1200°C, and three cycles were performed for each processing.

**Characterization:** Crude and calcined samples (conventional, simple microwave and hybrid microwave processing) were characterized using X Ray Fluorescence Spectrometry (XRF), Scanning Electron Microscopy (SEM) and Differential Scanning Calorimetry (DSC) techniques.

## RESULTS AND DISCUSSION

Table 1 presents the results of XRF analysis for pigment samples calcined using the conventional process (gas kiln).

**Chemical Composition (% mass)**

| Pigment | $Fe_2O_3$ | $Cr_2O_3$ | ZnO | NiO | CoO | L.I. |
|---|---|---|---|---|---|---|
| Black | 29,0 | 33,0 | - | 26,0 | 11,0 | 1,0 |
| Brown | 37,0 | 37,0 | 26,0 | - | - | - |

*Table 1 – Chemical composition determined by X Ray Fluorescence Spectrometry.*

Using the crude pigments, samples were prepared for each process. Each pigment was calcined in a conventional kiln and by microwave irradiation, for simple and hybrid processes. The DSC curves for crude and calcined samples are shown in Figures 1 and 2, for black and brown pigments, respectively. Thermal analysis (DSC) was used to determine the efficiency of the calcination process for each pigment. Reaction peaks in temperatures lower than the incongruent points (e.g., $T_g$, $T_m$, etc.) would indicate that the analyzed material is still reactive, i.e., the calcination process was incomplete. Thus, the more stable powders would present less reactivity, indicating the more efficient calcination process. For both pigments the process of more efficient calcination is the intermittent kiln (curves 1b and 2b, Figures 1 and 2, respectively), an effect more evident for the black pigment.

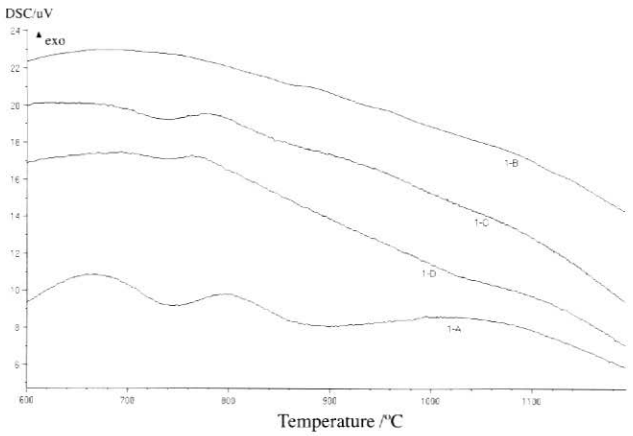


*Figure 1. Thermograms for the black pigment (CrFeCoNi system) crude (1a), processed in the intermittent kiln (1b), by simple microwave process (1c) and by hybrid microwave process (1d).*

For this pigment, the crude sample presents a reaction beginning at 670°C, probably associated with the energy necessary to make the pigment inert (curve 1a). Both simple and hybrid microwave irradiation process still present reactions in this temperature (curve 1c, simple microwave, and curve 1d, hybrid microwave). The sample calcined in intermittent kiln (curve 1b) does not present any reaction, demonstrating that the material has complete calcination.

For the brown pigment, the crude sample presents a reaction at 760°C (curve 2a), due to the material calcination. All three calcination processes (intermittent kiln, and simple and hybrid microwave irradiation) were apparently efficient; not having reaction peaks associated with calcination processes (curves 2b, 2c and 2d). However, the sample calcined in the intermittent kiln presents a reaction at 1140°C (curve 2b). Due to the peak form there is probably some phase change of the material.

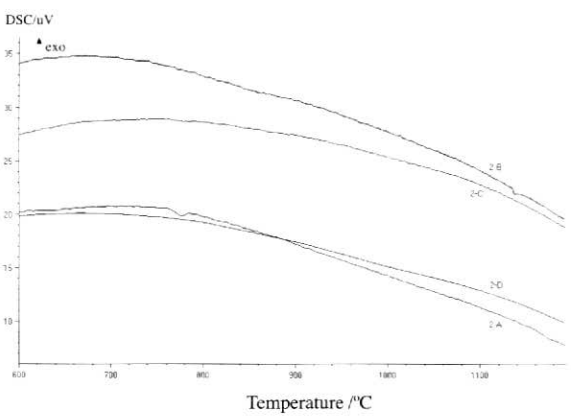


*Figure 2. Thermograms for the brown (CrFeZn system) crude pigment (2a), processed in the intermittent kiln (2b), by the simple microwave process (2c) and by the hybrid microwave process (2d).*

Micrographs obtained by SEM comprise the DSC results. The crude samples of black and brown pigments are presented as agglomerations of small particles, Figures 3 and 4, respectively. On the other hand, samples calcined in the intermittent kiln are presented as small and well-dispersed particles with defined geometry, showing the conventional calcination completely rounded particles (Figures 5 and 6).

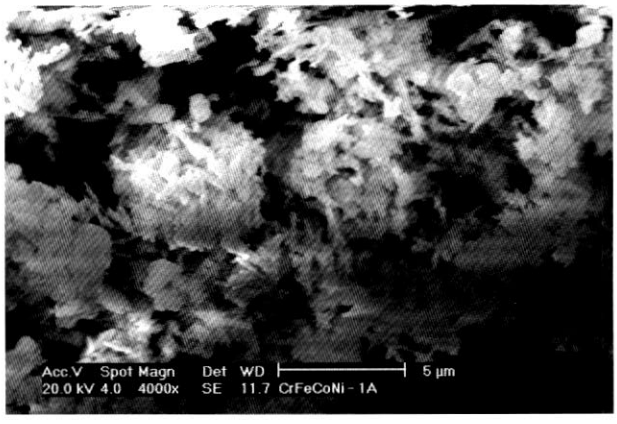


*Figure 3: Micrograph showing the black (CrFeCoNi system) crude pigment (not calcined).*

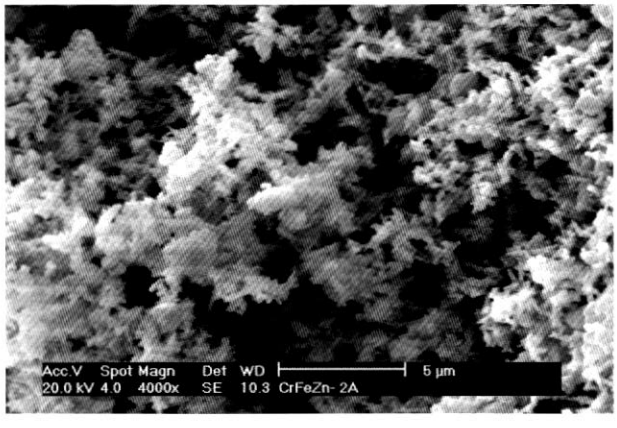


*Figure 4: Micrograph showing the brown (CrFeZn system) crude pigment (not calcined).*

Analyzing the micrographs for the conventional calcined pigments, it is observed that some particles have the appearance of small crystals, suggesting they underwent surface crystallization; however, reaction peaks were not observed in the associated thermograms (Figures 1 and 2), which could indicate the temperatures of crystalline structure formation. The probable crystallization of these powders could only be proven by X ray diffraction techniques.

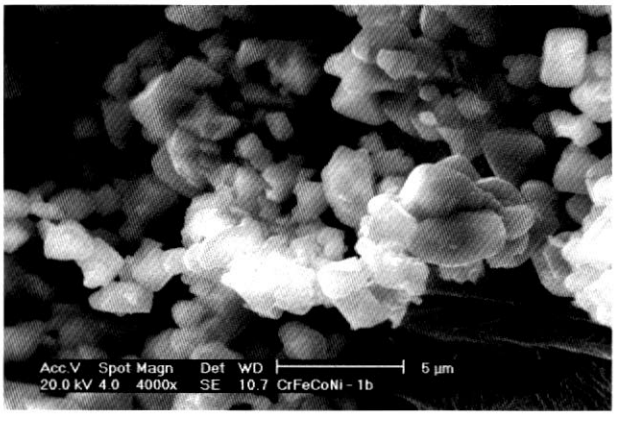


*Figure 5: Micrograph showing the black (CrFeCoNi system) pigment processed in the intermittent kiln.*

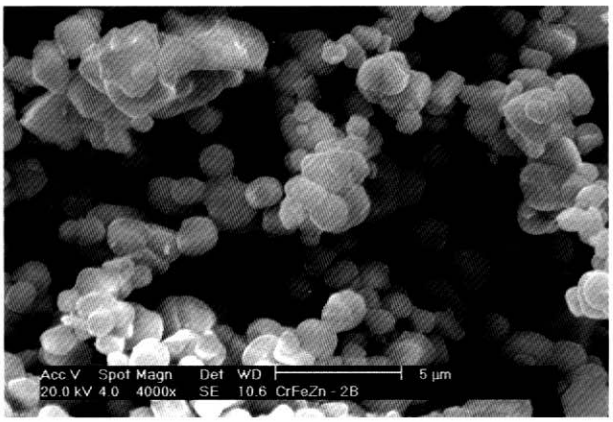


*Figure 6: Micrograph showing the brown (CrFeZn system) pigment processed in the intermittent kiln.*

The micrographs relative to both simple and hybrid microwave irradiation processes, for the black and brown pigments (Figures 7, 8, 9 and 10), show agglomerations with different proportions between non uniform particles and particles with definite geometry (rounded particles, indicating complete powder calcination). This fact demonstrates that the microwave processing was not effective, because there are calcined particles mixed with non-calcined ones. However, it must be observed that the cycles used for calcination in each process were very different; a period of 16h was used for the intermittent kiln (conventional process) and 12min (maximum) for the microwave process (simple and hybrid), apparently an insufficient amount of time to calcine the pigments studied.

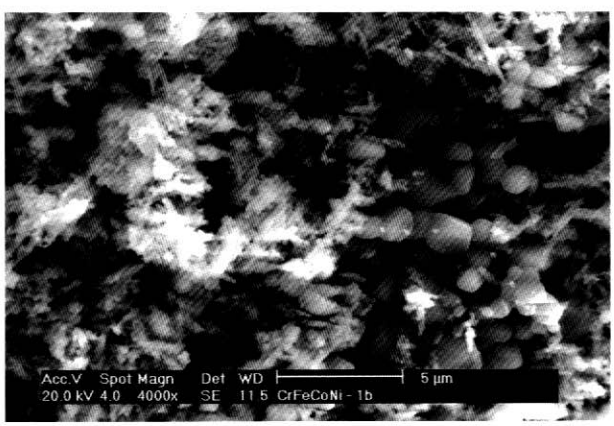


*Figure 7: Micrograph showing the black (CrFeCoNi system) pigment processed by simple microwave irradiation.*

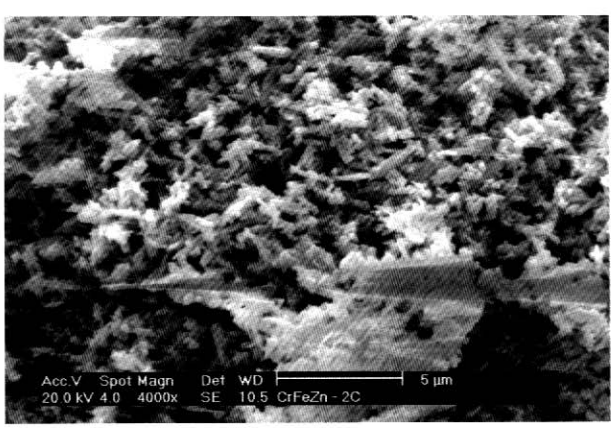


*Figure 8: Micrograph showing the brown (CrFeZn system) pigment processed by simple microwave irradiation.*

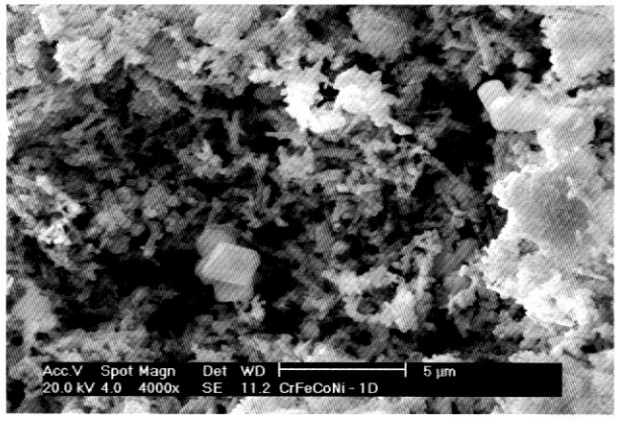


*Figure 9: Micrograph showing the black (CrFeCoNi system) pigment processed by hybrid microwave irradiation.*

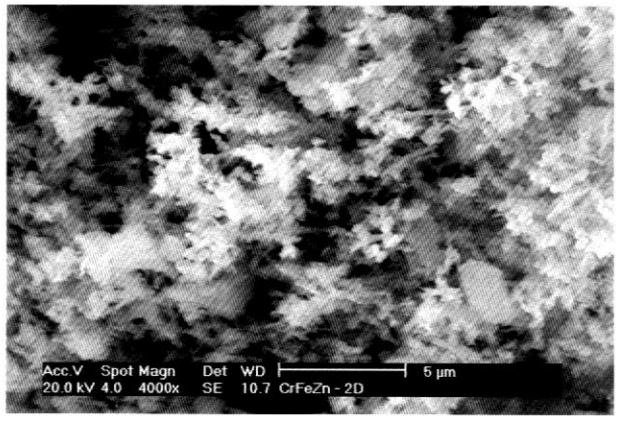


*Figure 10: Micrograph showing the brown (CrFeZn system) pigment processed by hybrid microwave irradiation.*

## CONCLUSIONS

The ceramic pigment preparation under microwave irradiation, for both simple and hybrid (30% microwave) processing, revealed itself as a promising technique for fast calcination, providing the materials processed with specific properties as a function of the interaction of these materials with the generated electromagnetic field in the microwave reactor. However, it demonstrated low efficiency since the pigments processed had not been completely calcined. Process optimization depends on the study of the interaction between microwave radiation and the material being processed in terms of its temperature and density, among other properties. It was verified that the samples calcined in the conventional mode, using an intermittent kiln, presented the best properties in relation to the stability of the pigments. However, it must be emphasized that this process took 16h relative to the total time of 6min~12min for the microwave irradiation process.

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