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Iron zircon pigment synthesis: Proposal of a mixing index for the raw materials mixtures

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ABSTRACT

Iron zircon coral pigments are very interesting from an industrial point of view because of their high colouring power and their stability at high temperatures. However, the pigment's synthesis is particularly troublesome due to its specific reaction mechanism. As an encapsulated pigment it becomes very important how the raw materials are distributed in the reaction mixture. To evaluate the effectiveness of the mixing process, it would be convenient to define a parameter, that is the mixing index, to estimate the degree of homogeneity of the system. In the current investigation, a mixing index is proposed derived from the power spectrum of Fourier transform of scanning electron microscope (SEM) images of the raw material mixture. Concretely, the number of pixels in a certain range of values in the image of the power spectrum, seems to behave relatively well as mixing index. This index allows us to distinguish between samples with different zirconia and iron oxide used as precursors. The proposed mixing index seems to be related to the colouring power of the final pigment when the synthesis generates enough zircon to encapsulate hematite particles.

Síntesis del pigmento de hierro-circón: Propuesta de un índice de mezclado para mezclas de materias primas

Palabras clave:
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Pigmento
Microestructura
Síntesis
Fourier

RESUMEN

Los pigmentos coral de hierro-circón son muy interesantes desde el punto de vista industrial ya que n un alto poder colorante y estabilidad a altas temperaturas. Sin embargo, la síntesis del pigmento es particularmente problemática debido a su mecanismo de reacción. Al tratarse de un pigmento encapsulado, resulta fundamental cómo se encuentran distribuidas las materias primas en la mezcla de reacción. Para evaluar la efectividad del proceso de mezclado, es conveniente definir un parámetro, que es el índice de mezclado, para estimar el grado de homogeneidad del sistema. En el presente trabajo de investigación se propone un índice de mezclado basado en el espectro de potencia de la transformada de Fourier de imágenes obtenidas con el microscopio electrónico de

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barrido de las mezclas de materias primas. Concretamente, el número de píxeles en un cierto rango de valores en la imagen del espectro de potencia parece funcionar relativamente bien como índice de mezcla. Este índice permite distinguir entre muestras con diferentes circonas y óxidos de hierro uitilizados como precursores. El índice de mezcla propuesto se relaciona con el poder colorante del pigmento final cuando durante la síntesis se genera suficiente cantidad de circón para encapsular las partículas de hematites.

Introduction

The zirconium iron coral pigment (Colour Pigments Manufacturers Association number code 14-44-5) is one of the most important zircon-based pigments (together with the zircon-vanadium blue and the zircon-praseodymium yellow) due to its colour intensity and thermal stability up to 1380 °C in all types of glazes [1–4]. Many authors suggest that the presence of hematite inclusions in the zircon matrix is the main responsible for the pigment's colour [3,5–8].

The traditional ceramic synthesis of iron coral pigment starts with a mixture of an appropriate hematite precursor with zirconia, silica and different mineralizers [9]. The stoichiometry of zircon synthesis is very simple, but the presence of mineralizers and the chromophore in the industrial synthesis of coral pigment implies a complex mechanism. It has been proposed that silica can be transported in both liquid phase and gas phase to the zirconia particles' surface, depending on the operating conditions, where it reacts. However, no transport mechanism has been described for hematite. Considering that the zircon synthesis and the hematite encapsulation must be simultaneous processes, the iron coral manufacture is particularly difficult due to many variables that affect the formation process of the protective zircon shell around hematite particles [10–13]. Obviously, the spatial distribution of raw material's particles is very important and it is related to the pigment's colouring power. Fig. 1 schematizes the hypothetical recommendable spatial distribution of the raw material's particles.

Numerous studies propose that the iron coral formation is influenced by factors such as the synthesis method, the precursors used in the composition and the mixing or milling process [6,13–19]. Additionally, particle's properties of the raw materials as size, density, shape, morphology and resilience are related to the homogeneity and reactivity of the system [20].

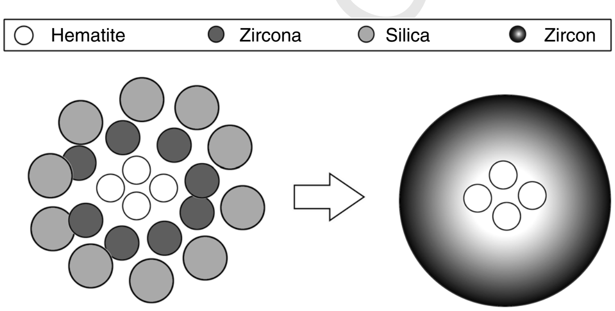

Fig. 1 – Recommendable spatial distribution of the particles in the mixture.

To evaluate the effectiveness of the mixing process, it would be convenient to define an easily measurable parameter as a mixing index, to estimate the degree of homogeneity of the raw material's mixture. Most mixing indexes proposed in the literature [21] were developed for binary mixtures and were based on statistical parameters, mostly the standard deviation or variance among samples drawn from a mixture. However, such indexes depend largely on the size as well as on the number of samples taken from the mixture. Indeed, many authors as Lacey or Poole [22,23] tried to establish a relation between the coefficient of variation and the sample size in a mixture. Their results demonstrate the dependence of homogeneity and the degree of randomness of the mixture on sample size, as well as the effect of the sample size on the mixing index.

Furthermore, the study of systems with several components with different particle size distribution is a complicated task because the mathematics involved are often quite complex and, on the practical side, the calculations are very tedious and require matrix manipulation and computer-based methods [21,24–27].

In a different approach, Shin and Fan [28] published a paper describing the applicability of the signal processing for the characterization of solid's mixtures. Concretely, the Fourier transform of the images obtained from a mixture of components could be employed to define a mixing index, evaluating some characteristics of the power spectrum of the transform (power spectrum is defined as a representation of the magnitude of the various frequency components of a 2D image that has been transformed with the Fourier transform algorithm from the spatial domain into the frequency domain [29]). In addition, the power spectrum obtained from the Fourier transform has a more interesting physical meaning that some statistical parameters listed above such as the standard deviation. The results obtained demonstrated how power spectrum of an image could be used as mixing index and studied the relationship between the homogeneity of a solids mixture and its power spectrum. Furthermore, this index allowed distinguishing between mixtures whose components were randomly distributed and ordered mixtures, that is, with segregated components. Nevertheless, this research was based on mathematical models and theoretical cases, without reference to real systems.

As it has been stated, the Fourier transform is one of the image-processing tools that can help to interpret homogeneity in a solids mixture, and when digital images are used, the Discrete Fourier Transform (DFT) can be applied. This method decomposes an image into its sine and cosine components,