

CoAl_{2-x}Cr_xO₄ BLACK CERAMIC PIGMENTS FROM POLYESTER RESINS. COMPARISON WITH THE CERAMIC METHOD

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The development of black pigments in ceramics entails serious problems with regard to keeping the colour steady, relating to the particle-size distribution of the powdered stain, its microstructure and the degree of reaction achieved in heat-treatment.

Spinel is one of the host structures par excellence in the field of ceramic pigments given the versatility of incorporating into the structure diverse colouring cations and modifiers. The American DCMA lists 15 compositions whose formulations are environmentally acceptable; the spinel of composition CoAl_{2-x}Cr_xO₄ is coded DCMA 13-29-2 with blue-greenish to black colours. Structurally it involves the miscibility of the spinel CoAl₂O₄ (normal spinel $\lambda=0$) and CoCr₂O₄ (also spinel $\lambda=0$).

In the present study the mixed spinel was obtained by two alternative synthesis procedures, the traditional ceramic method by oxide interdiffusion without using mineralisers (corundum, eskolayta and natural Co₃O₄ spinel) homogenised in a ball mill, and a polyesterification method involving precursor chlorides with tartaric acid -ethylene glycol. In this method the dissolved precursors were complexed in tartaric medium, which was polyesterified by controlled addition of ethylene glycol and slow water evaporation. The resulting resin was subjected to carbonisation at 250°C to develop a carbonaceous material, in which the precursor cations are molecularly mixed.

The powders underwent heat-treatment at 1000°C/6h. The starting microstructures of the unfired materials were studied, determining the arising crystalline phases and their crystal cell measurement by X-ray diffraction (XRD) and the UV-V spectrum of the glazed micronised powder in a transparent, lead-free glaze for porous single firing.

Table I details the results obtained by XRD and the measurement of unit cell parameters by POWCAL and LSQC software.

The data highlight the high reactivity of the polyester sample. Moreover, the cell

parameter measurement indicates a rise compared to that of CoAl_2O_4 , which suggests the entrance of Cr^{3+} in solid solution (Pauling radius $0.69\text{\AA}$) greater than Al^{3+} ($0.50\text{\AA}$).

Sample	T(°C)/6h	XRD	ASTM paratemers CoAl ₂ O ₄ 10-0458 a=b=c	Measured parameters
CERAMIC	600	Al ₂ O ₃ (d)Co ₃ O ₄ (m) Cr ₂ O ₃ (d)		
	1.000	CoAl ₂ O ₄ (f)		
POLYESTER	600	CoAl ₂ O ₄ (m)		
	1000	CoAl ₂ O ₄ (f)	8,103	8,161(4)

PEAK INTENSITY: f(strong), m(medium), d(weak).

Table I. Results obtained.

The polyester developed bluer hues than the ceramic material. Analysis of the optical spectra by the Tannabe Sugano model and lattice parameter measurements allowed interpreting the differences in colour in the two pigments on the basis of the introduction of more chrome at the octahedral site in the case of the polyester.

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