$CoAl_{2-X}CR_XO_4$ 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 $CoAl_{2-x}Cr_xO_4$ is coded DCMA 13-29-2 with blue-greenish to black colours. Structurally it involves the miscibility of the spinel $CoAl_2O_4$ (normal spinel λ=0) and $CoCr_2O_4$ (also spinel λ=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 Co_3O_4 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 0.69Å) greater than Al^{3+} (0.50 Å).

Sample	T(°C)/6h	XRD	ASTM paratemers $CoAl_2O_4$ 10-0458 a=b=c	Measured parameters
CERAMIC	600	Al_2O_3(d)Co_3O_4(m) Cr_2O_3(d)		
	1.000	$CoAl_2O_4$(f)		
POLYESTER	600	$CoAl_2O_4$(m)		
	1000	$CoAl_2O_4$(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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