ECONOMIC-ENVIRONMENTAL OPTIMISATION OF THE SPINEL COMPOSITIONS USED AS BLACK CERAMIC PIGMENTS

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1. INTRODUCTION

Royal Decree 2216/1985 (BOE 9 May 1986) approving the Regulations on the Declaration of New Substances and Classification, Packaging and Labelling of Hazardous Substances, Modified by Royal Decree 363/1995 (BOE 5-6-95), has acquired greater significance in view of the need for adequate risk evaluation in the use of chemical substances, as laid down in the bill of 31/1995 on the Prevention of Labour Risks. Furthermore, the need to minimise hazardous waste in accordance with the hierarchy of management set forth in the bill of 10/1998 on Wastes makes it necessary to develop products with a smaller hazardous materials content.

The manufacture of ceramic materials is not one of the most polluting activities or one that requires using hazardous substances. However, both economic and environmental reasons encourage reducing the use of hazardous, usually expensive substances, and replacing these by other, cheaper, less polluting ones.

In this sense, cobalt is being used to develop black pigments typically in the form of Co_3O_4 with RTECS (Registry of Toxic Effects of Chemical Substances) GG 2500000, harmful pictograph (Xi), and warnings on safety and care R 43, S 24-37.

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[1]. DRY COLORS MANUFACTURER'S ASS., DCMA *Classification and Chemical Description of the Mixed Metal Inorganic Coloured Pigments*, 2n. de, Washington DC, 1982.

[2]. T.A.S. FERREIRA, M.M.H. MENDONÇA, M.R. NUNES, F.M. COSTA, *A compartaive Study of $Co_xFe_{3-x}O_4$ (x=2) Spinel samples Obtained by Different Low Temperature Preparation Methods;* N. JOUINI, F. FIÉVET, I. ROSENMANN, *Magnetic Characterization of Ultrafine Cobalt Ferrite Particles Synthesized by a New Chemical Route,* Proceedings of VI European Conference in Solid State, Madrid, 1999.

2. EXPERIMENTAL

In the present work, a study was undertaken to minimise cobalt in the cobalt ferrite spinel across the whole range of Co substitution by Mg, so as to substitute Co_3O_4 by periclase MgO, which is not very toxic or pollutant. As precursors, industrial grade Fe_2O_3 hematite materials supplied by J.J. Navarro were used as a source of iron. The compositions prepared were: $Mg_xCo_{1-x}Fe_2O_4$ with x=0/0.2/0.5/0.7 and 0.9.

The mixtures were processed by the traditional method and heat treated at temperatures ranging from 800 to 1200°C. The resulting powders were characterised by different techniques:

(a) X-ray diffraction: the samples exhibited a single phase when fired at 1200°C except for x=0.9 which presented very weak hematite peaks, while at lower temperatures residual periclase was found in all the samples. Figure 1 shows the evolution of the synthesised spinel unit cell at 1200°C, indicating that the substitution of Co by Mg obeys Vegard's law.

(b) Scanning electron microscopy: Figure 2 depicts the micrograph of sample x=0.5 with spherical particulates sized between 1-2 μm. Part of these agglomerated and some agglomerates sintered to monoliths. The mapping suggests that some sintered materials were rich in Co and others in Fe, while there were also some regions exhibiting the presence of magnesium.

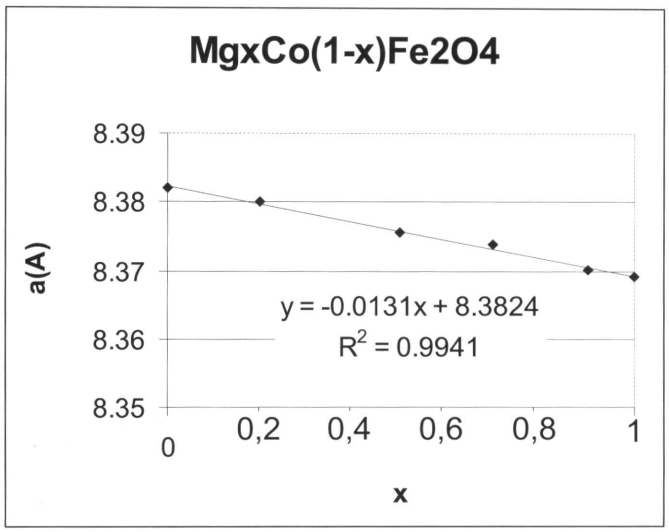

Figure 1. Variation of the spinel unit cell with x.

x (Mg)	L*	a*	b*
0	28,1	0,0	-2,7
0,2	28,5	-0,2	-1,8
0,5	**29,8**	**-0,6**	**-0,1**
0,7	31,2	-0,3	1,8

*Table 1. CIEL*a*b* differential colorimetry data.*

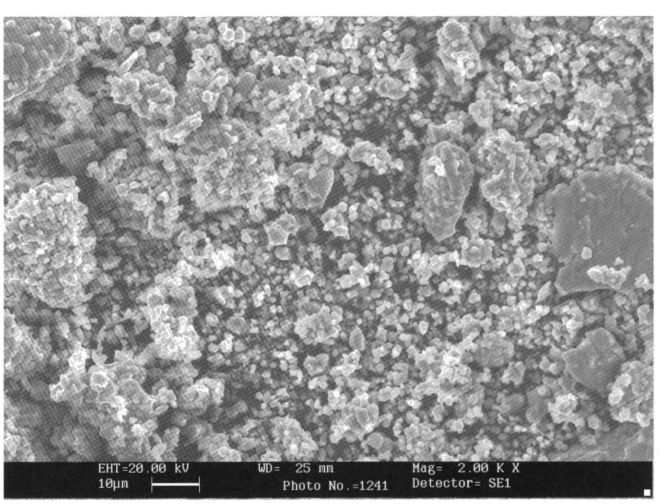

Figure 2. Electronic micrograph of sample x=0.5.

(c) The calcined, washed powders were used as glaze constituents in conventional ceramic glazes at a 5% content. The CIE-L*a*b* coordinates of the resulting glazed specimens were measured. The data are given in Table 1. The glazes at 5% turned blue with x=0.2 and 0.0, the blackest was x=0.5, while x=0.3 was greyish. Kubelka Munk studies indicate good general absorbency behaviour except in the red area (650-800 nm): on comparing these with a commercial colour made with

Fe,Co,Ni,Mn, values around 7 (6.5-7.7) were obtained in this wavelength range, and for the studied binaries the level was 1.5-3.5 without anything noteworthy being observed in this area.

3. CONCLUSIONS

The results indicate that Vegard's law is obeyed in the solid solution and they confirm the possibility of reducing the quantity of cobalt by substitution with magnesium, even with enhanced colour strength and a positive overall economic balance of the substitution. The introduction of this cation thus reduces the resulting product's toxic materials content.

ACKNOWLEDGEMENTS

The authors wish to thank CICYT for funding this work through project MAT 98-0392.