WASTE PREVENTION PLAN IN THE CERAMIC INDUSTRY. DECREASE IN LEVEL OF HAZARD AS REDUCTION INDICATOR

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ABSTRACT

*The new regulations on occupational heath (Law 35/1995 on labour risks), and on waste prevention (RD 952/1997 on hazardous wastes), introduce practices for reducing hazardous agents. The present paper sets out the possibility, in ceramic colourant production, of replacing the chromophore cations of metals of relative toxic risk (Ni, Co) by low toxicity metals (Mg, Al) in the case of black colouring spinels. For this, based on the colorimetric strength of the best commercial black pigments made with a notable presence of Ni, Co and Cr, and values CIEL*a*b*=33/1/0, the development was studied of solid solutions of inert forms in the base spinels $CoFe_2O_4$ and $NiFe_2O_4$ in their tetrahedral and octahedral positions. This substitution is effected without reducing their colouring strength and enables decreasing the quantity of hazardous material required in production as well as abating the hazard level and environmental impact of the wastes.*

1. INTRODUCTION

The new Valencia law on wastes 10/2000 (DOGV 15 December) follows the course of RD 952/97 on hazardous wastes, and in its Additional Provision 4, establishes that within a year of coming into force (before 16-3-2002), and in four yearly periods, waste producers in the Valencia Region shall present a plan for the prevention and reduction of wastes, expressly setting out: (a) objectives for reducing, assessing and quantifying these, (b) measures to be taken to achieve this, (c) evaluation and control system to attain the objectives.

In accordance with a precedent on waste prevention, RD 782/1998 Regulation for Application of the law on packings and packing waste 11/1997, minimisation indicators could include: (a) reduction of the quantity of arising waste per production unit, (b) rise of the reusable waste fraction compared with the non-reusable fraction, (c) physico-chemical improvement of materials and raw materials to enable reducing their hazard or minimising the environmental impact of the waste, (d) elimination of superfluous materials or raw materials, (e) increase of materials or raw materials whose wastes can more readily be assessed, including recycling, (f) rise in the quantity of recycled ceramic waste used in producing new ceramic materials.

2. OBJECTIVES

The present study sets out the possibility, in ceramic colourant production, of replacing the chromophore cations of metals of relative toxic risk (Ni, Co) by low toxicity metals (Mg, Al) in the case of black colouring spinels [1]. This substitution occurs without reducing their colouring strength and enables decreasing the amount of hazardous materials needed in production as well as reducing the level of hazard and environmental impact of the wastes.

The black spinels employed as black ceramic pigments are complex structures that use a group of transition cations located in the B octahedral and A tetrahedral positions of the structure AB_2O_4: A,B=Ni^{2+}, Co^{2+}, Mn^{2+}, Fe^{3+}, Cr^{3+}. In this list, Ni is considered as a heavy metal in European regulations (Commission Decision 2000/532/CE of 16-1-2001), confirmed carcinogen in human beings in its insoluble components (level A1 on the ACGIH scale with TWA of 0.2 mg/Nm^3 as Ni in labour environments), in its inorganic forms cobalt is carcinogenic in animals though this is not probable in human beings (level A3 on the ACGIH scale with TWA of 0.02 mg/Nm^3 as Co in labour environments). Chromium is a confirmed carcinogen in human beings as a chromate or Cr(VI) (level A1 on the ACGIH scale with TWA of 0. mg/Nm^3 in labour environments), but this form is unusual in ceramics where it is found and handled as Cr(III) (classified as A4, which indicates that data have not shown carcinogeneity in human beings or animals, and with TWA of 0.5 mg/Nm^3 as Cr in labour environments with inorganic forms). Manganese (TWA of 0.2 mg/Nm^3 as Mn in labour environments with inorganic forms) and iron (TWA of 1 mg/Nm^3 as Fe in labour environments with soluble forms) present few eco-toxicological problems [2,3]. The presence of ionic forms of nickel or cobalt are considered hazard-contributing components in the wastes that contain them (codes C5 and C4 respectively in RD 952/97 on hazardous wastes of 5-7-97). The reduction of both ions in formulating black pigments therefore involves a reduction in their degree of hazardousness in processing, handling and waste management.

The present work has studied the substitution of Ni and Co ions by inert ions such as Mg, Al or Zn and the minimisation of chromium in the formulation [4,5,6,7]. For this, based on the colorimetric strength of the best commercial black pigments L*a*b*=33/1/0, the development was studied of solid solutions of inert forms in the base spinels $CoFe_2O_4$ and $NiFe_2O_4$ in both their tetrahedral and octahedral positions.

2. EXPERIMENTAL

First, a wide survey was conducted of commercial black pigments, with a view to establishing the compositional typology employed and the particle size characteristics. After establishing the commercial formulations and their pigmenting strength in ceramic bases, systems were formulated optimising the generally formulated spinel $A(B_2)O_4$ or $B(AB)O_4$ for standard or inverse spinel respectively, indicating in brackets the cations occupying the octahedral position. Black pigment preparation was designed using two base compositions [4,6]:

(A) NICKEL BLACKS

Trevorite or ferrite of nickel base $Fe(NiFe)O_4$. In principle it was attempted to avoid this formulation in view of the greater hazard of nickel compounds mentioned above.

(B) COBALT BLACKS

Cobalt ferrite base Fe(CoFe)O_4. A formulation is involved that decreases the hazard of the former while holding the other necessary co-chromophores.

The formulations were optimised on the basis of three variables or criteria:

(a) colouring strength must match that of the present commercial product

(b) preparation conditions and resulting microstructure must be similar to commercial ones

(b) the presence of Ni must be minimised.

(c) if it is possible to do without nickel, the presence of cobalt and chromium must be minimised.

The samples were prepared from their oxides: NiO, Co_3O_4, Cr_2O_3, Fe_2O_3, ZnO, MgO, AlO(OH) supplied by J.J. NAVARRO, of industrial quality. The powders were mixed in a planetary mill using acetone as dispersion medium and after drying they were calcined in an electric kiln. The calcined powders were manually micronised and sieved before use as a 5% colourant addition to a conventional frit used in monoporosa cycles.

Therefore, in the different optimisations, the CIEL*a*b* co-ordinates were measured of 5% pigment additions to a conventional monoporosa base. X-ray diffraction (XRD) powder analysis was performed to evaluate the crystalline phase present as well as the size of the unit cell by using an internal standard (α-alumina) and fitting the diffraction peaks by least squares [8]. Furthermore, the samples were studied by SEM-EDX to determine their spot composition and particle size characteristics.

3. STUDY OF BLACK COMMERCIAL SPINEL PIGMENTS

Four black colourants marketed in the Castellón ceramic sector by different suppliers were studied. Table I details the results of the characterisations run on these four materials.

SAMPLE	**L*a*b***	**XRD**	**SEM**	**EDX (FeCrNiCo)** mol/formula
1	32,6/0,9/-0,4	2 phase spinel	Particulate 0.5-1 μm. 4 μm. quartz	Nickel-cobalt ferrochromite $(1\,1\,{}^{1}/_{2}\,{}^{1}/_{2})$ Manganese cobaltite
2	33,0/1,0/0,0	single-phase spinel	Particulate 1 μm aggregates	Nickel-cobalt ferrochromite $(1\,1\,{}^{2}/_{3}\,{}^{1}/_{3})$
3	32,6/0,8/-0,4	single-phase spinel	Particulate 1-2 μm aggregates	Nickel-cobalt-manganese ferrochromite $(1\,1\,{}^{2}/_{3}\,{}^{1}/_{3})$
4	32,6/0,8/-0,4	single-phase spinel	Particulate 1 μm	Nickel-cobalt-manganese ferrochromite $(1\,1\,{}^{1}/_{2}\,{}^{1}/_{2})$

Table I. Characterisation of the commercial pigments analysed.

Table I shows that the different formulations achieve a similar pigmenting level in all the materials. There are single-phase spinel pigments and also two-phase spinel pigments. Chromium is introduced in all the formulations (approximately 1 mol/formula by weight) and always nickel and cobalt, albeit in varying quantities. No manganese was added in just one pigment. Particle shape is irregular and mean sizes do not exceed 2 μm, typical values being 1 μm (Figure 1). Pigmenting strength in the conventional monoporosa base is similar in each and of the order of L*a*b*=33/1/0.

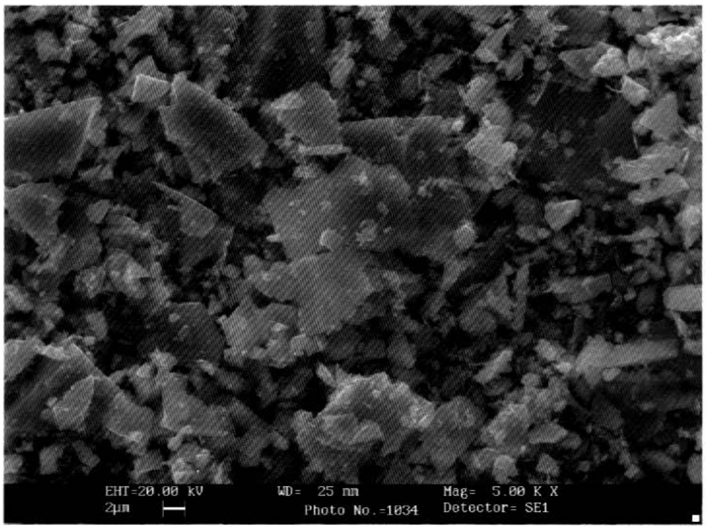

Figure 1. Micrograph of commercial pigment 2.

4. Fe(NiFe)O_4 NICKEL BLACKS

These pigments were optimised according to the following steps: (a) optimisation of the minimum quantity of chromium required in an octahedral gap to achieve optimum colour, (b) optimisation of the maximum quantity of inert magnesium that can replace nickel without reducing colouring strength, (c) optimisation of the maximum quantity of magnesium and zinc that can replace nickel without reducing colouring strength, (d) introduction of aluminium to replace iron in the foregoing optimisation. The optimisations are discussed below.

4.1. OPTIMISATION OF THE MINIMUM QUANTITY OF CHROMIUM NEEDED IN AN OCTAHEDRAL GAP TO ACHIEVE OPTIMUM COLOUR

Figure 2 shows the results of the evolution of a* and b* as well as lattice parameter a with degree of substitution x on preparing the solid solutions $Ni(Fe_{2-x}Cr_x)O_4$ at 1300°C/6h, at which the samples were calcined, since at 1200°C/6h the samples x>0.9 exhibited unreacted chromium oxide in XRD; at 1300°C all the samples exhibited trevorite as single phase, indicating full solid solution $NiFe_2O_4$-$NiCr_2O_4$. The values of L* in all the samples are around 28.

Figure 2 shows that the values of a* and b* approach the zero value of the abscissa starting at x=1. Moreover this abscissa x=1 is the minimum observed for the cell edge.

In accordance with the stabilisation energies of the crystalline field (157.6 KJ/mol for $Cr^{3+}(d^3)$, 86.2 KJ/mol for $Ni^{2+}(d^8)$ and 0 for Fe^{3+}(d5)), Cr will situate itself in the octahedral position, first displacing Fe, so that solid solution $x<1$ has the form $Fe(NiFe_{1-x}Cr_x)O_4$. However, when all the iron has been displaced by chromium, nickel will be replaced, which will take up the tetrahedral positions in the lattice, that is, if $x>1$ the solution is $Fe_{2-x}Ni_{x-1}(Ni_{2-x}Cr_x)O_4$. In the first case, the smaller chromium causes shrinkage of the network shown in Figure 2.b, but on exceeding x=1 the entry of nickel in tetrahedral positions is accompanied by expansion of the network.

At levels $x>1$ the value L*a*b*=28/0,8/-2 differs from that of commercial black 33/1,0/0,0 by $\Delta=(\Delta L^{*2}+\Delta a^{*2}+\Delta b^{*2})^{1/2}= 5.3$, which means that it is a similar black, slightly bluish and a little more intense.

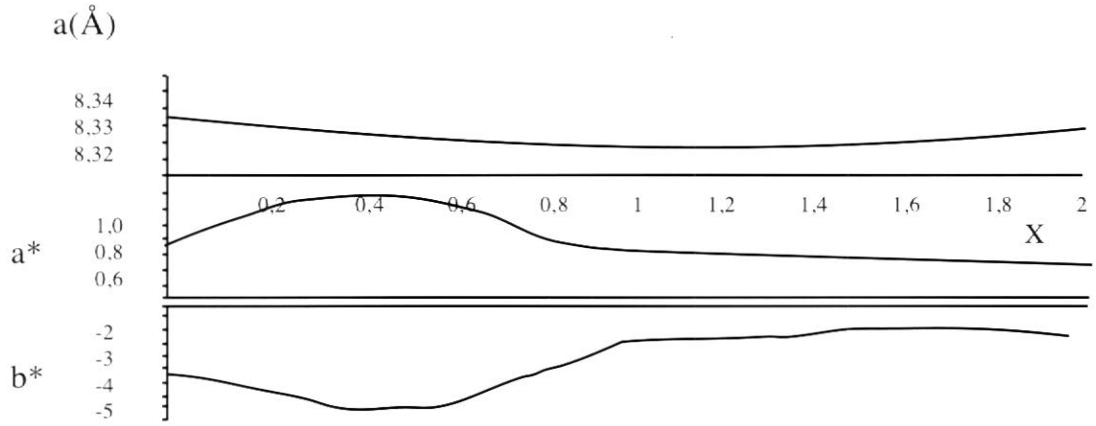

Figure 2. Results of the characterisation of samples $Ni(Fe_{1-x}Cr_x)O_4$ at 1300°C/6h of 4.1: evolution of cell parameter and evolution of colorimetric parameters a and b*.*

4.2. OPTIMISATION OF THE MAXIMUM QUANTITY OF INERT MAGNESIUM THAT CAN SUBSTITUTE NICKEL

In the previous study the stoichiometric proportion Fe:Cr appeared to be the minimum chromium to achieve black colorations similar to the multi-component commercial blacks. In view of the little chromophoric significance of the tetrahedral position, Ni was formally replaced by inert Mg; in fact, given the stabilisation in the crystalline field of Ni^{2+}, nickel will remain in an octahedral position and it will be iron that moves to octahedral positions replacing nickel, according to the scheme $Fe_{1-x}Mg_x(Ni_{1-x}Fe_xCr)O_4$.

Table II sets out characterisation data of these samples calcined at 1200°C/6h, unlike those of section 4.1, which were calcined at 1300 to produce a single phase in the entire series. It can be observed that at 1200°C sample x=0 improves slightly compared with its counterpart calcined 1300 in 4.1. Moreover, the samples x=0.2 (L*a*b*=28,5/2,3/1,9) and 0.4 exhibit glaze colorations with differences Δ with x=0 of just 0.9 and 1.3 respectively; i.e., the colour is held with substitutions of x=0.4 and certainly in x=0.2 if it is considered that Δ=1 would be the colour tolerance limit, though the value of a* is relatively high compared with the colour optimised at 1300°C in 4.2 (L*a*b*=28/0,8/-2).

The measurements of the lattice parameters indicate a gradual increase in unit cell as is to be expected of a clear substitution of a small ion such as nickel(II) by magnesium.

x	XRD 1200ºC/6h	CIEL*a*b* Powder	CIEL*a*b* Glazed	A(Å)
0.0	T(480)	37.3/0,1/-02	28.2/1,7/1,3	8.309 ± 0.005
0.2	**T(450)**	**37.5/0,7/0,4**	**28.5/2,3/1,9**	**8.316 ± 0.003**
0.4	T(380)	38.5/1,5/1,1	29.0/2,6/1,7	8.327 ± 0.002
0.6	T(410)	38.6/3,1/2,4	29.0/3,5/2,4	8.333 ± 0.002
0.8	T(450)	39.2/3,2/1,7	29.8/4,3/2,7	8.347 ± 0.002
1.0	T(400)	40.6/6,1/3,7	31.4/7,0/4,4	8.350 ± 0.004

T(trevorite $NiFe_2O_4$), in brackets peak intensity, in cps, of the greatest relative intensity observed of the phase.

Table II. Characterisation of samples $Fe_{1-x}Mg_x(Ni_{1-x}Fe_xCr)O_4$*. of 4.2.*

4.3 OPTIMISATION OF THE MAXIMUM QUANTITY OF MAGNESIUM AND ZINC THAT CAN SUBSTITUTE NICKEL WITHOUT REDUCING COLOURING STRENGTH

In view of the substitution of 20% nickel by magnesium, to reinforce the absorption of long wavelengths it was attempted to substitute nickel by stoichiometric proportions of magnesium and zinc to decrease the browning of the samples (a*). Given the size of Zn(II) (0.89 A radius of Shannon and Prewit) [9], its foreseeable entry in the octahedral position ($Zn^{2+}(d^{10})$ does not provide a stabilisation of the crystalline field), it expands its co-ordination sphere causing the network to shrink, and therefore shrinking that of its adversary nickel(II), whose crystal field stabilisation will decrease and therefore, will absorb larger wavelengths, reinforcing the absorption of red and avoiding the browning of the samples [10].

For this, ceramic compositions $(Fe_{1-2x}Mg_xZn_x)$ $(Fe_{2x}Ni_{1-2x}Cr)O_4$ were prepared. The samples presented a single phase at 1200°C/6 h except for certain peaks of negligible intensity that are assigned with difficulty to a solid solution of iron-chromium hematite, also used as a black colourant for in-mass colouring of porcelain tile. Table III details the results of its characterisation: the entry of the relatively large zinc(II) and magnesium(II) replacing carcinogenic nickel is observed to increase cell size and the difference in colour is less than unity for x=0.1 (0.4) and for x=0.15 (0.7). It is therefore possible to produce similar black colours by substituting 30% of the nickel in the formulation (15% magnesium and 15% zinc).

x	XRD 1200ºC/6h	CIEL*a*b* Powder	CIEL*a*b* Glazed	a(Å)
0.0	T(275)C(20)	39,9/0,3/0,6	28.7/1,6/1,1	8.310 ± 0.004
0.1	T(220)C(15)	39,6/0,9/0,9	28,9/1,9/1,0	8.313 ± 0.004
0.15	**T(22)C(10)**	**39. /1,2/1,0**	**29.2/2.1/1,1**	**8.319 ± 0.003**
0.2	T(225)	39.2/1.8/1.4	29.2/2.8/1.7	8.322 ± 0.003

T(trevorite $NiFe_2O_4$), in brackets peak intensity, in cps, of the greatest relative intensity observed of the phase.

Table III. Characterisation of samples $(Fe_{1-2x}Mg_xZn_x)$ $(Fe_{2x}Ni_{1-2x}Cr)O_4$ *of 4.3.*

4.4 INTRODUCING ALUMINIUM TO REPLACE IRON IN THE FOREGOING OPTIMISED COMPOSITION

In order to try and improve component a* of the colour (around 2 in the previous optimised formulations compared with 1 in the commercial pigment), samples were prepared by doping the composition optimised in 4.3 according to the scheme $(Fe_{0,8}Mg_{0,1}Zn_{0,1})(Fe_{0,2}Ni_{0,8}Cr_{1-x}Al_x)O_4$.

Table IV details the results found with these samples. Colour is not observed to improve, residual hematite always appears doped with chromium in the samples and the cell parameter does not alter with x. This indicates that the solid solution has not been produced and aluminium has not entered into the network.

x	XRD 1200ºC/6h	CIEL*a*b* Powder	CIEL*a*b* Glazed	a(Å)
0.0	T(210)C(50)	39,9/0,9/07	29,3/1,9/-0,3	8.319 ± 0.003
0.02	T(260)C(15)	40,0/0,8/0,7	29,0/1,7/-0,1	8.322 ± 0.004
0.05	T(205)C(10)	40,2/0,8/0,8	29,1/2,0/0,5	8.319 ± 0.003
0.075	T(235)C(15)	39,8/0,9/0,7	29,2/2,1/0,6	8.318 ± 0.003
0,1	T(195)C(15)	39,8/0,8/0,6	28,9/1,7/0,3	8.317 ± 0.003
0,2	T(190)C(10)	40,1/1,0/0,8	28,8/1,9/0,5	8.315 ± 0.004

T(trevorite $NiFe_2O_4$), in brackets peak intensity, in cps, of the greatest relative intensity observed of the phase.

Table IV. Characterisation of samples $(Fe_{0,8}Mg_{0,1}Zn_{0,1})(Fe_{0,2}Ni_{0,8}Cr_{1-x}Al_x)O_4$ *of 4.4.*

5. $Fe(CoFe)O_4$ COBALT BLACKS

In accordance with the literature, black spinel pigments can be developed without nickel in the formulation, though this approach is not adopted in the current commercial pigments studied, perhaps owing to lack of incentives for diminishing the hazards of materials and products.

The health-focused optimisation of the pigment was designed with a cobalt ferrite base, an inverse spinel given the $Co^{2+}(d^7)$ octahedral crystalline field stabilisation, in the following steps. (a) optimisation of the maximum quantity of cobalt replaceable by inert magnesium, (b) optimisation of the minimum quantity of chromium in octahedral position in the optimum product with magnesium, (c) optimisation of the maximum quantity of inert aluminium in solid solution substituting iron in the optimum product by magnesium, (d) optimisation of the composition with the minimum chromium needed in the composition optimised with magnesium and aluminium.

5.1 OPTIMISATION OF THE MAXIMUM QUANTITY OF COBALT REPLACEABLE BY INERT MAGNESIUM

Compositions were prepared formally substituting cobalt by magnesium, which due to the well-known crystal field stabilisation effect involves a substitution mechanism indicated by $(Fe_{1-x}Mg_x)(Co_{1-x}Fe_{1+x})O_4$. The calcination studies indicate that at 1000ºC/6h the samples $x<0.5$ exhibit spinel as single phase, but with more magnesium, MgO periclase and Fe_2O_3 hematite remain non-reacted; on recalcining these at 1200ºC/6h, all the samples exhibit a fully developed spinel phase, indicating a complete solid solution of magnesium in the network.

Table V details the results of the characterisations of the samples. It can be observed that sample x=0.5 (L*a*b* = 29,8/-0,6/-0,1) has colour levels that exceed both the optimised commercial composition (33/1,0/0,0) and x=0 (28,1/0,0/-2,7) with values Δ=3.2: the sample would be a more intense black than the commercial product and less bluish than x=0 without magnesium. The cell shrinks with the substitution that obeys a classic Vegard law of substitution by size.

x	**XRD** 1200°C/6h	**CIEL*a*b*** Glazed	**a(Å)**
0.0	F(360)	28.1/0,0/-2,7	8.3820 ± 0.0005
0.2	F(380)	28,5/-0,2/-1,8	8.3801 ± 0.0007
0.5	F(370)	29.8/-0,6/-0,1	8.3757 ± 0.0004
0.7	F(415)	31,2/-0,3/1.8	8.3738 ± 0.0005
0,9	F(333)H(35)	brown	8.3702 ± 0.0003
1,0	F(200)H(90)	brown	8,375± 0.001

F(spinel phase x=0 $CoFe_2O_4$ and x=1 $MgFe_2O$)H(hematite). In brackets peak intensity, in cps, of the greatest relative intensity observed of the phase.

Table V. Characterisation of samples $(Fe_{1-x}Mg_x)(Co_{1-x}Fe_{1+x})O_4$ *of 5.1.*

5.2 OPTIMISATION OF THE MINIMUM QUANTITY OF CHROMIUM IN OCTAHEDRAL POSITION IN THE OPTIMUM COMPOSITIONS WITH MAGNESIUM

With a view to adjusting reactivity samples were prepared calcined directly at 1200°C of the series $(Mg_{0,5}Fe_{0,5})(Cr_xCo_{0,5}Fe_{1,5-x})O_4$. Table VI lists the characterisations of the series, showing that sample x=0 presents non-reacted periclase as was to be expected, on not having been precalcined at 1000°C as in the series discussed in 5.1. The entry of chromium in the composition raises the reactivity of the system and additions exceeding x=0.1 do not improve the colour developed.

x	**XRD** 1200°C/6h	**CIEL*a*b*** Glazed	**a(Å)**
0.0	F(345)MgO(20)	38,5/-0,1/0,0	8.3792 ± 0.0004
0.1	**F(380)**	**32,0/1,0/0,9**	**8.3755 ± 0.0002**
0.2	F(370)	32,1/1,1/0,9	8.3377 ± 0.0003
0.5	F(415)	32,6/1,1/-01	8.3745 ± 0.0008

F(spinel phase $MgFe_2O$). In brackets peak intensity, in cps, of the greatest relative intensity observed of the phase.

Table VI. Characterisation of samples $(Mg_{0,5}Fe_{0,5})(Cr_xCo_{0,5}Fe_{1,5-x})O_4$ *of 5.2.*

Figure 3 shows the microstructure of the sample with chromium and with x=0.2. In the sample without chromium, particulate appears of 1-2 μm mean size with irregular shapes, as well as agglomerates and sometimes sintered particles. The EDX study by mapping indicates that cation distribution is non-uniform in the sample: some particles are richer in cobalt and others in magnesium. On introducing chromium into the composition, the microstructure exhibits smaller size particles (1 μm), with a smaller degree of agglomeration and without forming sintered materials (Fig. 3 x=0.2); moreover particles appear homogeneous without cation deaggregation when studied by mapping. Chromium therefore appears to have an important effect on reactivity and microstructure. However, additions exceeding x=0,1 fail to enhance the coloration and the microstructural appearance is similar. On comparing sample x=0.1 (32/1,0/0,9) with the commercial compositions (33/1,0/0,0) it exhibits Δ=1.4 being slightly more intense though with slight yellowing.

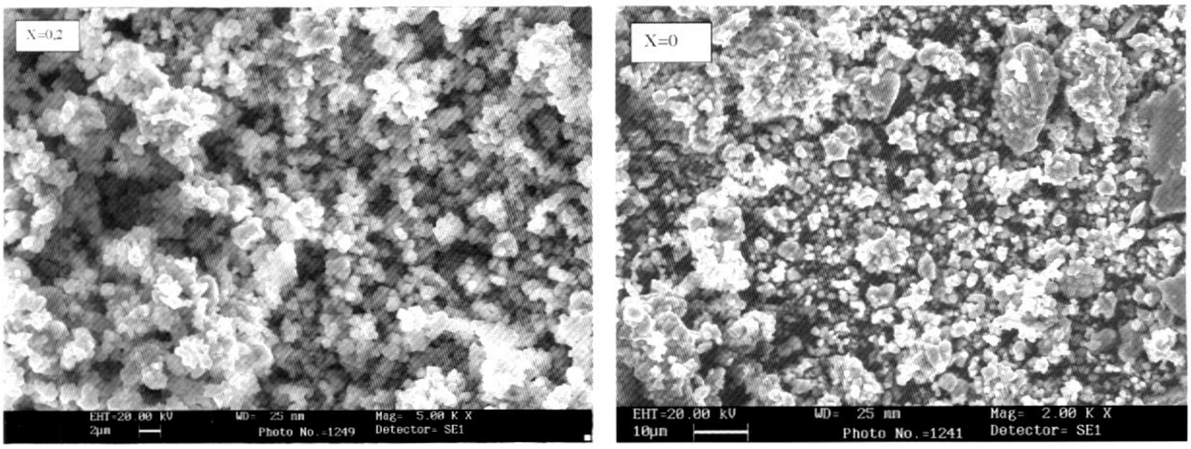

Figure 3. Micrograph of sample x=0.2 and x=0.

5.3 OPTIMISATION OF THE MAXIMUM QUANTITY OF INERT ALUMINIUM IN SOLID SOLUTION IN THE OPTIMISED COMPOSITION WITH MAGNESIUM

In order to study the effect of the entry in the octahedral position of aluminium, the series $(Mg_{0,5}Fe_{0,5})(Al_xCo_{0,5}Fe_{1,5-x})O_4$ was studied, which entails a clear substitution of iron by the small Al^{3+}. The network relaxing effect caused by the entry of aluminium means a better interaction of the ligand field with regard to its adversaries Co^{2+} and Fe^{2+}, with the ensuing rise in stabilisation energy of the crystalline field and decrease in the absorption wavelengths, with a shift toward blue (b* negative cancelling the previous yellowing).

Table VII gives the characterisation data of these samples. In this case, on calcining at 1200°C the samples show the presence of residual periclase in x=0; samples x=0.1 and 0.2 have a single phase and x=0.5 contains the iron aluminate spinel together with the solid solution spinel phase. The colorimetric results indicate an important drop in colour intensity compared with the samples with chromium in the foregoing section, but in contrast present the sought shift to blue (b*=-1).

x	XRD 1200ºC/6h	CIEL*a*b* Glazed
0.0	F(345)MgO(20)	38,5/-0,1/0,0
0.1	F(280)	33,5/-0,1/-0,5
0.2	**F(275)**	**34,9/-0,4/-1,0**
0.5	F(210)$FeAl_2O_4$(40)	34,9/-0,4/-1,3

F(spinel phase $MgFe_2O$). In brackets peak intensity, in cps, of the greatest relative intensity observed of the phase.

Table VII. Characterisation of samples $(Mg_{0,5}Fe_{0,5})(Al_xCo_{0,5}Fe_{1,5-x})O_4$ *of 5.3.*

5.4 OPTIMISATION OF THE COMPOSITION WITH THE MINIMUM CHROMIUM REQUIRED IN THE COMPOSITION OPTIMISED WITH MAGNESIUM AND ALUMINIUM

Though the entry of aluminium avoids a certain yellowing of the colour, strength decreases. To combine both effects composition x=0.2 with aluminium in section 5.3 was selected, and samples were prepared introducing chromium in the series $(Mg_{0,5}Fe_{0,5})(Al_{0,2}Co_{0,5}Fe_{1,3-x}Cr_x)O_4$, effectively substituting iron by chromium in the octahedral position.

Table VIII sets out the characterisation data of the samples. Calcination at 1200°C/6h repeats the previous results and in all the samples only the spinel phase is detected. From a colorimetric viewpoint, sample x=0.06 increases in 3 points the intensity of the sample without chromium and now the value b* is only 0.1. Comparing this sample (L*a*b*=30,0/0,7/0,1) with the optimised commercial composition (33,0/1,0/0,0) clearly demonstrates obtainment of a very **similar, stronger colour with a difference of Δ=3 owing to the increase in intensity.**

x	XRD 1200°C/6h	CIEL*a*b* Glazed
0.0	F(200)	33,0/-0,8/-1,9
0.06	**F(270)**	**30,0/0,7/0,1**
0.10	F(180)	29,5/0,9/0,3
0.14	F(210)	30,0/1,0/0,2

F(spinel phase $MgFe_2O$). In brackets peak intensity, in cps, of the greatest relative intensity observed of the phase.

Table VIII. Characterisation of samples $(Mg_{0,5}Fe_{0,5})(Al_{0,2}Co_{0,5}Fe_{1,3-x}Cr_x)O_4$ *of 5.4.*

6. CONCLUSIONS

The results of the study allow drawing the following conclusions:

(a) In the commercial black pigments with a spinel structure, it is common to find a broad ranging formulation with the presence of Ni^{2+},Co^{2+},Cr^{3+},Fe^{3+},Mn^{2+}. In this list, Ni is considered a heavy metal according to European regulations (Commission Decision 2000/532/CE of 16-1-2001), confirmed carcinogen in human beings in its insoluble components (level A1 on the ACGIH scale with TWA of 0.2 mg/Nm³ as Ni in labour environments), in its inorganic forms cobalt is carcinogenic in animals though this is not probable in human beings (level A3 on the ACGIH scale with TWA of 0.02 mg/Nm³ as Co in labour environments). Chromium is a confirmed carcinogen in human beings as a chromate or Cr(VI) (level A1 on the ACGIH scale with TWA of 0. mg/Nm³ in labour environments), but this form is unusual in ceramics where it is found and handled as Cr(III) (classified as A4, which indicates that data have not shown carcinogeneity in human beings or animals, and with TWA of 0.5 mg/Nm³ as Cr in labour environments with inorganic forms). Manganese (TWA of 0.2 mg/Nm³ as Mn in labour environments with inorganic forms) and iron (TWA of 1 mg/Nm³ as Fe in labour environments with soluble forms) present few eco-toxicological problems [2,3].

(b) The black commercial pigments analysed exhibit a similar pigmenting strength with 5% additions to a conventional monoporosa frit and CIEL*a*b* values around 33,0/1,0/0,0.

(c) The lack of incentives for decreasing cations with greater occupational and environmental hazards leads ceramic colour producers to avoid addressing the issue of reducing these agents in their formulations in a decisive fashion. The new regulations on occupational heath (Law 35/1995 or labour risks), and on waste prevention (RD 952/1997 on hazardous wastes), should introduce this type of practices for reducing hazardous agents in pigment factories.

(d) This reduction is possible and has been demonstrated in the case of black colouring spinels.

(e) It is possible to produce a base spinel $Fe(NiFe)O_4$ decreasing 30% of the nickel, substituting this by inert magnesium and zinc $(Fe_{0,7}Mg_{0,15}Zn_{0,15})$ $(Fe_{0,3}Ni_{0,7}Cr)O_4$. However, it is necessary to keep high proportions of chromium in the formulation. The CIEL*a*b* colorimetric values lie around 29,2/2,1/1,1 with improved intensity compared with the commercial products studied, though exhibiting more browned hues.

(f) It is possible to produce a spinel free of nickel in the system $Fe(CoFe)O_4$, and decrease the quantity of cobalt in the formulation by 50% on replacing this by inert magnesium. Furthermore, chromium only needs to be introduced in 0,06 mol/formula by weight according to the composition $(Mg_{0,5}Fe_{0,5})(Al_{0,2}Co_{0,5}Fe_{1,24}Cr_{0,06})O_4$. With a 5% addition, this pigment produces a CIEL*a*b* colour in the glassy monoporosa matrix of 30/0,7/0,1, which improves on the intensity of the commercial colourants analysed.

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