

Environmental study of $\text{Cr}_2\text{O}_3\text{--Al}_2\text{O}_3$ green ceramic pigment synthesis

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Abstract

A green pigment was synthesised based on a $\text{Cr}_{2-x}\text{Al}_x\text{O}_3$ solid solution, using a standard ceramic industry composition with and without different mineralisers and using raw materials industrial grade reagents. The resulting products were compared with a pigment made using chemically pure (CP grade) to establish the most appropriate reagents for achieving minimum Cr(VI) segregation during the pigment washing stage, and comparable chromatic qualities to those of a standard industrial pigment. Chromium sesquioxide was used as Cr(III) precursor instead of a Cr(VI) compound, and the chromium content was also optimised. The X-ray photoelectron spectroscopy (XPS) results indicated that a solid solution only forms when CP grade reagents are used. This is consistent with the scanning electron microscopy (SEM) and X-ray diffraction (XRD) data obtained in the study. Smaller Cr(VI) and B contents were found in the washing liquids when CP grade reagents were used, but the resulting chromatic quality was slightly lower than that of a standard pigment made and used in the ceramic industry.

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1. Introduction

Cr-doped structures have been widely studied as ceramic pigments.^{1–3} Chromium depending on synthesis conditions, it can be found in different states of oxidation (II–VI) and these generate different properties, stability and coloration. This difficulty in understanding the colouring mechanism, and the few related studies found in the literature, have led to undertaking this study on chromium contain pigmenting systems, trying to keep the Cr(III) ion from oxidising to Cr(VI) because of its negative environmental impact, since it will be segregated to the washing waters.⁴

Cr(VI) is taken into your body through the respiratory system (the handling of Cr(VI) precursors by workers), water or food (due to irrigation with polluted water) and can cause acute gastroenteritis, allergic dermatitis, chronic conjunctivitis, rhinopharyngitis and lung cancer.

Thus, a factor to be kept in mind is the handling of Cr(VI) precursors. The National Institute of Occupational Health and Safety recommended that the chromium (VI) compound quantity handled should not exceed 1 mg/m^3 during 10 working hours a day.^{5–9}

A series of patents on the synthesis of this pigment can be found in the literature,^{10–13} in all of which a highly toxic carcinogen Cr(VI) compound is used as chromium precursor. The mineralisers used in synthesis also often contain toxic components.

Cr_2O_3 and Al_2O_3 are sesquioxides having the same corundum crystal structure, which is approximately hexagonal, involving close-packed oxide ions with the Cr^{3+} and Al^{3+} ions occupying two thirds of the available octahedral sites. According to the $\text{Cr}_2\text{O}_3\text{--Al}_2\text{O}_3$ phase diagram,¹⁴ these two oxides can form a complete range of substitutional solid solutions between the solidus temperatures, $\sim 2100^\circ\text{C}$ and $\sim 950^\circ\text{C}$, which can be formulated as $\text{Cr}_{2-x}\text{Al}_x\text{O}_3$ ($0 \leq x \leq 2$). An immiscibility dome is present below 950°C , which contains two crystalline phases (alumina-rich and chromia-rich solid solutions), but the actual decomposition of a homogeneous solid solution into two phases takes place very slowly.

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Colouring ranges from green to red, depending on the chromium content. To produce a green colouring pigment, the Cr_2O_3 content needs to exceed that of Al_2O_3 . As the quantity of aluminium rises, the crystal field increases, owing to the smaller size of aluminium compared with chromium, producing a shift in the absorption bands to higher energies and a pink colour, which is the case of ruby. This was the first laser system to be discovered and more than 20 years later, it is still important.

In the ceramic industry, a pigment based on a $\text{Cr}_{2-x}\text{Al}_x\text{O}_3$ composition is used, in which $x=0.77$ ($\text{Cr}_{1.23}\text{Al}_{0.77}\text{O}_3$). The pigment produces a green colour, and could be included in group III of the DCMA classification.¹⁵ However, the high temperatures required for pigment synthesis constrain its preparation and use, so that certain additives (known as mineralisers) need to be used to lower synthesis temperature.

This pigment is usually synthesised by the conventional ceramic method, involving mixture-dispersion of the metal oxides in a planetary ball mill and heat treatment of the mixture at temperatures above 1300 °C for solid-state reaction. This procedure presents some drawbacks. As the product formation rate is controlled by slow diffusion processes,¹⁴ high reaction temperatures are required, with the entailing energy cost. These high temperatures produce volatile reagent losses and hence departure from starting system stoichiometric conditions. To improve these interdiffusion processes, small quantities of various additives are introduced that provide a fluid phase through which reactions can proceed without the activation energy barrier found in the solid-state process.

As far as we know, such additives can have the following effects:¹⁶

1. On melting at temperatures below pigment formation temperature, these additives could provide a liquid medium and increase the diffusion rate between the reagents, thereby speeding up the reaction,
2. They can act on particle size. This is very important since the sintering rate is roughly proportional to the inverse of particle size, which controls end colour.
3. If an additive ion is able to replace a pigment chromophore ion, colour strengthening can occur owing to modification of crystalline field

intensity. Colour is often, but not always associated with d–d electronic transitions.

However, it is very difficult to study the action of mineralisers because despite the usefulness of phase diagrams in establishing the temperature and composition range in which certain phases or mixtures of phases can exist under thermodynamic equilibrium conditions, they fail to show all the effects of small compositional changes.

The aim of the present work was the study of a green ceramic pigment based on a $\text{Cr}_{2-x}\text{Al}_x\text{O}_3$ solid solution, which contains chromium as a chromophore element. Results of this pigment were compared with a commercial pigment (STD). The specific objectives were:

- elimination of Cr(VI) and halogens as precursors,
- study of different mineralisers as well as their optimisation,
- obtaining a ceramic pigment with better values of the chromatic co-ordinates (L^*, a^*, b^*) than the commercial pigment,
- producing minimum concentrations of chromium (VI) in washing waters,
- study characteristics of the pigment synthesised with industrial materials and chemically pure materials.

2. Experimental procedure

2.1. Preliminary study

A preliminary study was first performed on the $\text{Cr}_{2-x}\text{Al}_x\text{O}_3$ composition produced using a standard ceramic industry composition, in which $x=0.77$ (sample VII), with and without different mineralisers, to establish the most suitable one(s) for reducing Cr(VI) segregation in washing liquids. To avoid handling various factors simultaneously, synthesis was performed at a fixed temperature (1000 °C for 2 h), at which the phase diagram indicated formation of a homogeneous solid solution.

Industrial grade Cr_2O_3 and Al_2O_3 were used as raw materials, and CP grade LiF, LiBO_2 and H_3BO_3 were used as additives. These particular mineralisers were chosen owing to their low melting points.

Table 1 lists the samples prepared. The mineralisers LiF, LiBO_2 and H_3BO_3 were incorporated in 2 wt.%

Table 1
Study of mineralisers for composition $\text{Cr}_{1.23}\text{Al}_{0.77}\text{O}_3$

Samples	VIIIM1	VIIIM2	VIIIM3	VIIIM2+3	VIIISM
$\text{Cr}_{2-x}\text{Al}_x\text{O}_3$	$x=0.77$	$x=0.77$	$x=0.77$	$x=0.77$	$x=0.77$
Mineralisers	2% LiBO_2	2% H_3BO_3	2% LiF	2% H_3BO_3 + LiF	–

additions, and a 1:1 mixture of LiF–H₃BO₃ was also tested, which was similarly incorporated in a 2 wt.% addition.

The mixtures were refined and homogenised in acetone in a planetary ball mill. After drying, the samples were fired in a Carbolite electric furnace at a heating rate of 10 °C/min to 1000 °C, with a 2 h soaking time. To refine and homogenise particle size after calcining, the resulting product was ground in an agate mill with acetone, followed by sieving at 50 µm.

To verify their compositional stability as ceramic colorants, 3% (w/w) of the calcined samples was applied onto ceramic bodies with an industrial frit whose composition did not contain Zn or Sn, to respectively avoid ZnCr₂O₄ spinel formation and pink shades. After drying, the pieces were fired in an electric kiln. The thermal treatment applied corresponded to a standard industrial ceramic tile firing cycle, and consisted of five steps: heating to 800 °C in 18 min, followed by heating from 800 to 1080 °C in 17 min, 5 min hold at 1080 °C, followed by cooling to 600 °C in 20 min, and finally cooling to room temperature in 15 min.

Phase analysis of the fired samples was performed by X-ray powder diffraction (XRD) with a SIEMENS D5000 diffractometer with Cu K_α radiation. Data were collected by step-scanning from 10 to 120° 2θ with a step size of 0.05° 2θ and 5 s counting time at each step at room temperature. The goniometer was controlled by the “SIEMENS DIFFRACT plus” software, which also determined diffraction peak positions and intensities. The instrument was calibrated using an external Si standard.

CIELAB colour parameters were determined at room temperature with a VARIAN UV/Visible spectrophotometer (Model CARY 500 SCAN) and a coupled analytical software for colour measurements. The data were registered from 380 to 700 nm using a PTFE blank as reflecting standard. CIELAB colour parameter measurements were conducted using a D65 standard illuminant. Colorimetry serves to characterise a colour and allow identification. In this system, *L** is the lightness axis [black (0) to white (100)], *a** is the green (<0) to red (>0), and *b** is the blue (<0) to yellow (>0) axis.^{17,18}

In view of the high carcinogen toxicity of Cr(VI) ions, the Cr (VI) content in the washing liquids of the samples was determined by a colorimetric method recommended by the EPA¹⁹ (Environmental Protection Agency). Thus 0.3 g fired sample was subjected to successive washings with hot 0.3M HNO₃ until obtaining 50 mL solution. Measurements were conducted on the spectrophotometer used for CIELAB measurements at 540 nm.

2.2. Compositional study

After establishing which mineraliser yielded the best colour and least Cr(VI) segregation in the washing

waters under the foregoing working conditions, the effect of chromium concentration on pigment colour was studied by means of three compositions, listed in Table 2. In the three samples, H₃BO₃ (2% w/w) was added as a mineraliser. As the purpose of the study was to produce a useful green pigment for the ceramic industry without Cr(VI) precursors, as well as suppressing this ion in washing processes, it was decided to conduct the study using industrial grade Cr₂O₃ and Al₂O₃. CP grade H₃BO₃ was used as an additive. Calcining temperatures were 1000, 1100, 1200 and 1300 °C with soaking times at each temperature of 2 and 6 h. The heating rate was 10 °C/min. In order to refine and homogenise particle size after calcining, the resulting product was ground in an agate mill with acetone, followed by sieving at 50 µm.

To verify their compositional stability as ceramic colorants, 3% (w/w) of the calcined samples was applied with an industrial frit. The thermal treatment used corresponded to a standard industrial ceramic tile firing cycle.

As in the preliminary study, the Cr(VI) content in the washing liquids was determined by the colorimetric method recommended by the EPA. CIELAB colour parameter measurements were run on the same spectrophotometer, under the same conditions as above.

2.3. Precursor study

After studying the effect of the mineraliser and optimising the chromium content for good green colour and minimum Cr(VI) segregation in the washing liquids, this composition, V2LM2, was synthesised with CP grade reagents. The results were compared with those of sample V2IM2, synthesised with industrial grade reagents, using the same work procedure and characterisation method set out above.

To determine the particle size of the industrial grade and CP grade raw materials, these underwent the same grinding process, prior to calcination, used in mixing and homogenising the compositions being studied. Particle size of the ground raw materials was measured in a Coulter LS230 with micro volume module. The particle-size range which can be determined by this instrument lies between 0.4 and 2000 µm.

The amount of Cr(VI) in the washing liquids was determined by the colorimetric method recommended by the EPA. CIELAB colour parameter measurements

Table 2
Different proportions of the raw materials

Samples	Composition
V1IM2	Cr _{2-x} Al _x O ₃ (x = 0.77) + H ₃ BO ₃ (2% w/w)
V2IM2	Cr _{2-x} Al _x O ₃ (x = 0.86) + H ₃ BO ₃ (2% w/w)
V3IM2	Cr _{2-x} Al _x O ₃ (x = 0.99) + H ₃ BO ₃ (2% w/w)

were run on the same spectrophotometer, under the same conditions as in the preliminary study.

As H_3BO_3 was used as a mineraliser in synthesising these samples, and the analysis of boron content in water can be very helpful from an environmental point of view since this element occurs in water as a result of industrial processes, particularly in the ceramic sector, the boron content in the washing liquids was analysed by the Azomethine-H method.²⁰

In these samples, the chromium oxidation state and chromium and aluminium contents were analysed by XPS. The XPS spectra were recorded on a VG-Escalab-210 electron spectrometer equipped with a multichannel detector. The spectra were excited by using the Mg K_{α} (1253.6 eV) radiation of a twin anode in the constant analyzer energy mode with a pass energy of 40 eV. To facilitate analysis of the samples, self-supporting wafers of 13 mm diameter were prepared, which were fixed on the sample holder. Samples were previously outgassed at 100 °C for 3 h in the preparation chamber of the spectrometer and subsequently transferred to the analysis chamber. The pressure of the main chamber was maintained at 3×10^{-10} mB. To avoid the damage induced by the X-ray radiation, samples were cooled at 173 K during the acquisition and the X-ray power was limited to 120 W (10 mA–12 KV). The spectral acquisition time was reduced to prevent damaging the sample. The binding energy (BE) scale was regulated by setting the C1s transition at 284.6 eV. The accuracy of the BE was ± 0.1 eV.

The surface composition was estimated from the corresponding XPS peak area ratios by using the relation:

$$\left[\frac{X}{Y}\right] = \frac{A_x \sigma_y \lambda_y}{A_y \sigma_x \lambda_x} \sqrt{\frac{E_k(X)}{E_k(Y)}}$$

where A , σ , λ and E_k are respectively the integral of each peak after S-shaped background subtraction, the effective ionization cross section, the escape depth and the photoelectron kinetic energy. Cross section values were taken from Scofield²¹ and the escape depth was calculated from the formulas given by Vulli and Starke.²²

Direct evidence of the external versus internal location of Cr and Al has been additionally obtained by carrying out XPS analysis of the exposed external surface of the particle.²³ Herein, we have combined this technique with progressive sputtering with a fast Ar^+ beam that produces increasing decapping of the external layers of the particles.²⁴ This enables mapping out the Cr and Al level from the exterior to the interior of the solid particle up to a depth of 100 Å. Maximum relative mistake of XPS measures is around 10%.

Scanning electron micrographs of the powder samples were taken on a scanning electron microscope (SEM) (Leica Leo 440) equipped with a spectrometer for energy-dispersive X-ray microanalysis (EDX), using the following operating parameters: acceleration voltage 20

KV, measuring time 100 s, working distance 25 mm, counting rate 1.2 Kcps. The samples for microstructural and microanalysis determination were placed in an aluminium holder and coated by graphite film.

Phase analysis of the unglazed samples was performed by X-ray powder diffraction (XRD) under the same conditions as in the foregoing preliminary study.

3. Results and discussion

3.1. Preliminary study

The XRD spectra of sample VII, studied with and without mineralises, exhibit peaks that are mainly assignable to Cr_2O_3 (JCPDS N° 38–1479), while there are also other small peaks that are attributable to Al_2O_3 (JCPDS N° 88–0107).

Fig. 1 depicts the values of the CIELAB $L^*a^*b^*$ co-ordinates corresponding to the studied solid solution of this composition after glazing, with and without the addition of different mineralises, together with those of a standard industrial pigment (STD). It can be observed that the values of the L^* co-ordinate are very similar in all the synthesised samples, indicating greater lightness than in the STD values. However, sample VIIM2 exhibits a^* and b^* values closer to those of the STD pigment.

Analysis of the Cr(VI) content in the washing waters, detailed in Table 3, indicates that composition VIIM2 segregates less Cr(VI) during washing. These results cannot be compared with those of the STD pigment

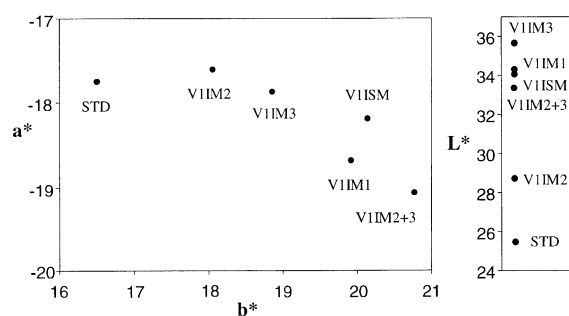


Fig. 1. CIELAB colour parameters of composition $Cr_{1.23}Al_{0.77}O_3$ (VII) with and without different mineralisers after glazing.

Table 3

Cr(VI) segregation in the washing waters of composition $Cr_{1.23}Al_{0.77}O_3$ (VII) with and without different mineralisers after glazing

Samples	mg Cr (VI)/g pigment
VIIM1	0.301
VIIM2	0.237
VIIM3	1.988
VIIM2 + 3	0.403
VIISM	1.627

because the industrial pigment was supplied washed. Therefore, a specific mineraliser is necessary to diminish the percentage of Cr(VI) in the washing waters.

These results suggest H_3BO_3 could be the best additive for synthesising this pigment, since although it exhibits no differences with the others as regards the X-ray diffractogram, the colorimetric parameters lie closer to those of the STD pigment and the Cr(VI) content in the washing liquids is lower. The effect of H_3BO_3 could stem from the fact that the B_2O_3 forming from H_3BO_3 during firing has a melting point around $450\text{ }^\circ\text{C}$. Boric oxide has a particularly useful effect in shortening melting and refining time (removal of gas bubbles). For this reason, boron is typically used as a flux to encourage fluidity by favouring ion interdiffusion processes and homogeneity in ion distribution, which encourages ion incorporation into the solid solution and avoids oxidation of Cr(III) to Cr(VI).

3.2. Compositional study

The CIELAB chromatic co-ordinate measurements after glazing (Fig. 2a and b) indicate that composition V2IM2 calcined at $1300\text{ }^\circ\text{C}$ for 2 h exhibits the best values, even surpassing those of the STD pigment.

As the samples calcined with a 6 h soaking time did not exhibit better chromatic co-ordinates than those calcined for 2 h, segregation in washing waters was only studied in the latter and this soaking time was subsequently used at each temperature in the rest of the study.

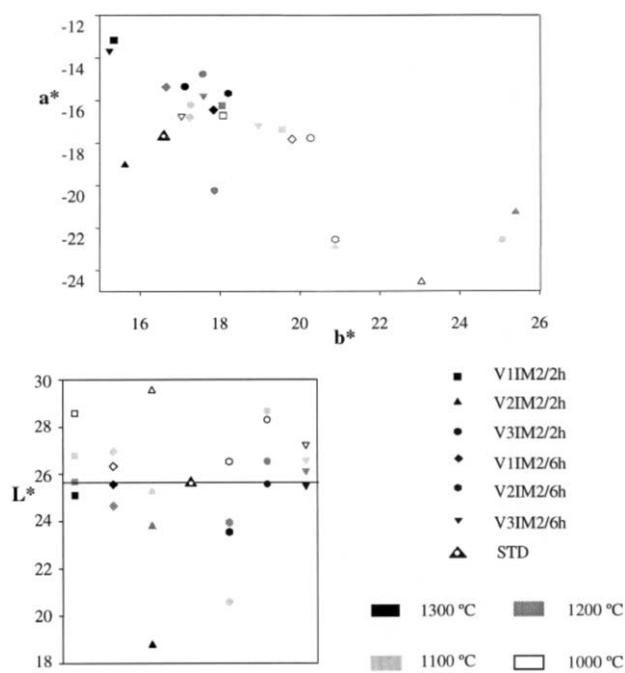


Fig. 2. CIELAB colour parameters of all the samples with 2 and 6 h soaking times after glazing: (a) a^* and b^* ; (b) L^* .

Analysis of Cr(VI) content in the washing liquids of different samples after calcination at each respective temperature for 2 h, depicted in Fig. 3, indicates that composition V2IM2 calcined at $1300\text{ }^\circ\text{C}$ segregates the smallest quantity of this ion in the washing liquids.

These data indicate that a green pigment can be produced with a lower starting chromium content, using Cr_2O_3 and not Cr(VI) compounds as precursors, which has improved chromatic co-ordinates compared with the STD pigment and segregates less Cr(VI) in the washing water. These findings are significant for the ceramic pigment industry, since they enable eliminating the toxicity involved in handling Cr(VI) compounds during the preparation stages, while also considerably reducing the quantity of these ions in the washing waters, a process stage with a very high environmental risk.

3.3. Precursor study

After the influence of the mineralisers and most appropriate quantity of chromium for good colouring and minimum Cr(VI) segregation in the washing waters using industrial grade raw materials had been studied, the $Cr_{2-x}Al_xO_3$ ($x=0.86$) composition, which was found to best match the objectives set, was synthesised using industrial grade reagents (V2IM2), followed by calcination at 1000, 1100, 1200 and $1300\text{ }^\circ\text{C}$ with a 2 h hold at these temperatures.

The results were then compared with the data found with the V2LM2 composition to observe the effect of the CP grade material.

As the starting reagents were of different quality, their particle size was determined first, after grinding under the same conditions used in mixing and homogenising the pigment ingredients.

The data indicate that both industrial and CP grade Cr_2O_3 particle sizes are quite similar, as Fig. 4a shows. This is however not the case with Al_2O_3 particle size. It can be observed in Fig. 4b that industrial grade Al_2O_3

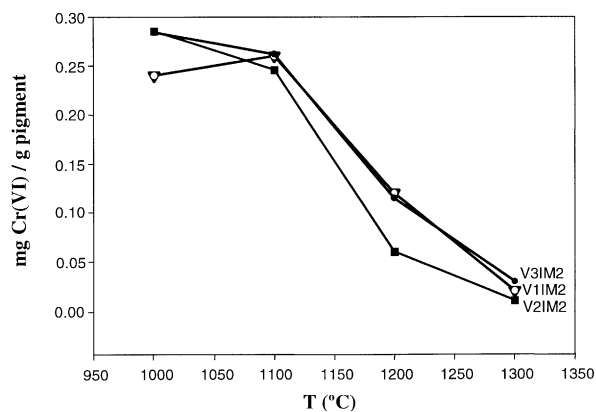


Fig. 3. Segregation of Cr(VI) with a 2 h soaking time in washing waters.

has a notably larger particle size, so that the Al_2O_3 grade used will undoubtedly affect sample reactivity.

Table 4 sets out the Cr(VI) contents in the washing liquids of the samples prepared after calcination at different temperatures. The data indicate that the samples prepared with industrial grade and CP grade reagents segregate less Cr(VI) at 1300 °C, and that composition V2LM2 is the best from an environmental standpoint, as it segregates less Cr(VI).

As this composition contains boron, added for its possible mineralising effect, which as mentioned above can also have adverse effects, the boron content was analysed in the washing liquids of the two samples calcined at 1300 °C for 2 h. The resulting were V2IM2 0.037 mg B/g pigment and V2LM2 0.012 mg B/g pigment. They show that sample V2LM2 segregates less boron.

In European legislation the permitted quantities for Cr(VI) in water emissions are between 0.2 and 0.5 ppm and for B segregation are between 2 and 10 ppm. It can be observed that emissions the quantities of Cr(VI) and B detected after washing the pigment made with indus-

trial grade raw materials (V2IM2) and the pigment made with CP grade reagents (V2LM2) are below limits.

To evaluate the chromatic properties of these two samples, the values of the CIELAB chromatic co-ordinates of the samples were determined after glazing with an industrial frit whose composition contained no Zn or Sn, and compared with those of the pigment (STD) used as a reference in this study. The results, detailed in Table 5, indicate that the sample prepared with industrial grade raw materials and synthesised under the same conditions as the sample made with CP grade reagents has a greater pigmenting strength, as the values of the L^* a^* b^* co-ordinates are closer to those of the STD pigment.

The compositions prepared with industrial and CP grade reagents, calcined at 1300 °C for 2 h, were analysed by XPS before and after washing them with HNO_3 0.3 M. The resulting data, given in Table 6, indicate a greater chromium content in the samples prepared with industrial grade reagents, both before and after washing. However, the aluminium content is larger in the samples made with CP grade reagents, and this generally decreases after washing. The rise in aluminium content in sample V2IM2 when this is washed can be

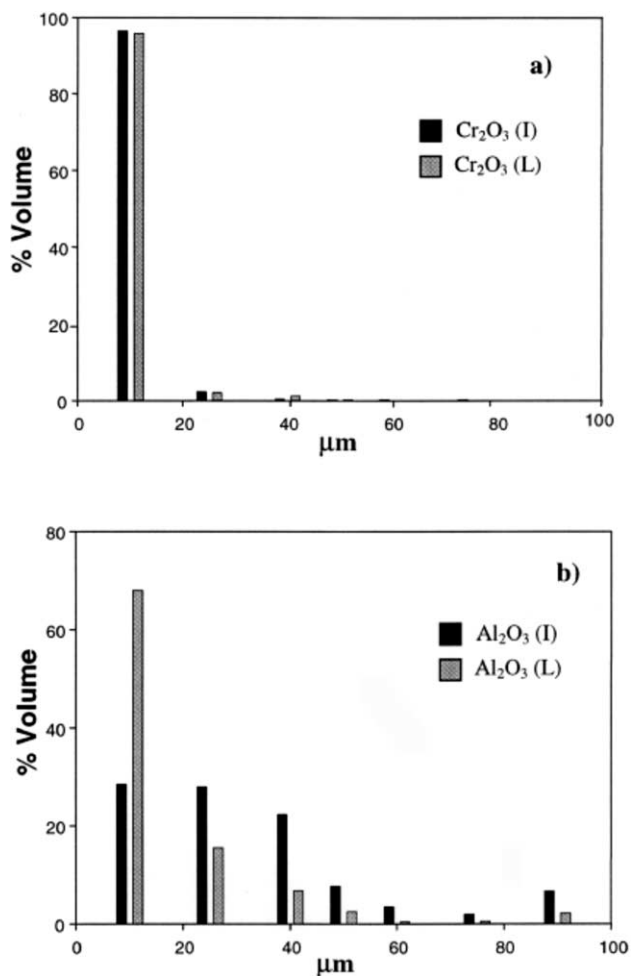


Fig. 4. Particle size: (a) industrial grade and CP grade Cr_2O_3 ; (b) industrial grade and CP grade Al_2O_3 .

Table 4
Cr(VI) segregation in the washing waters

Test temperature	SAMPLES	
	V2LM2	V2IM2
	mg Cr (VI)/g pigment	
1000 °C for 2h	0.0465	0.2854
1100 °C for 2h	0.0276	0.2457
1200 °C for 2h	0.0013	0.0627
1300 °C for 2h	0.0010	0.0176

Table 5
CIELAB colour parameters of the different raw materials after glazing

Samples	Glazed samples		
	a^*	b^*	L^*
V2LM2	-13.83	14.21	29.26
V2IM2	-19.02	15.63	18.78
STD	-17.75	16.50	25.75

Table 6
XPS of samples V2IM2 and V2LM2 (washed and non-washed) calcined at 1300 °C

SAMPLES	% Al	% Cr
Nominal starting content	17.2	21.5
V2IM2 (non-washed sample)	12.0	26.6
V2LM2 (non-washed sample)	21.3	17.0
V2IM2 (washed sample)	13.0	23.3
V2LM2 (washed sample)	19.7	14.3

due to the presence of Carbon masking its signal. The data suggest that chromium is incorporated more effectively in the Al_2O_3 network when reagents of greater purity are used. This would explain the chromium contents in the washing liquids, since if present as free chromium, chromium can be more readily removed in washing. It was also confirmed that chromium was present as Cr(III) in all the compositions analysed.

The SEM performed on sample V2IM2 calcined at $1300\text{ }^\circ\text{C}$ for 2 h, Fig. 5, indicates the presence of large particles, and chromium and aluminium mapping confirms that Al_2O_3 is involved, warranting the conclusion that chromium has not entered the alumina network and confirming the presence of a larger chromium content detected by XPS. However, the micrograph of sample V2LM2 calcined at $1300\text{ }^\circ\text{C}$ (Fig. 6), and the chromium and aluminium mapping indicate great homogeneity in chromium and aluminium distribution.

The XPS depth study regarding the atomic percentage of chromium and aluminium, shown in Fig. 7a, indicates that in sample V2IM2 calcined at $1300\text{ }^\circ\text{C}$ for 2 h, there is practically no variation in chromium and aluminium content. This is consistent with the SEM findings and confirms non-formation of a solid solution, so that the green colour must be due to Cr_2O_3 , leading, as experimentally determined, to greater chromium segregation in the washing liquids. An environmentally worse pigment is therefore involved.

The same depth study performed with sample V2LM2 calcined at $1300\text{ }^\circ\text{C}$ for 2 h, Fig 7b, indicates a decrease in the aluminium content and an increase in the chromium content with depth until converging at one point. This could indicate that aluminium is incorporated into the Cr_2O_3 network with the formation of a solid solution, as a result of which less free chromium is left, so

that a smaller quantity of chromium is detected in the washing waters.

The X-ray diffractograms of samples V2IM2 and V2LM2 after calcining at $1300\text{ }^\circ\text{C}$ for 2 h indicate that sample V2LM2 exhibits diffraction peaks assignable to Cr_2O_3 , which are slightly displaced towards higher 2θ values at $1300\text{ }^\circ\text{C}$ for 2 h, compared both with those of JCPDS file n° 38–1479 and those of the Cr_2O_3 used as a raw material and fired under the same conditions. This

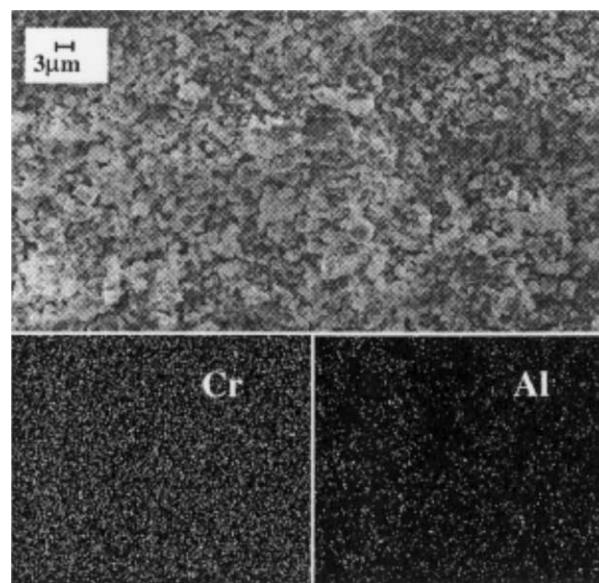


Fig. 6. Micrograph and chromium and aluminium mapping of sample V2LM2 calcined at $1300\text{ }^\circ\text{C}$ for 2 h.

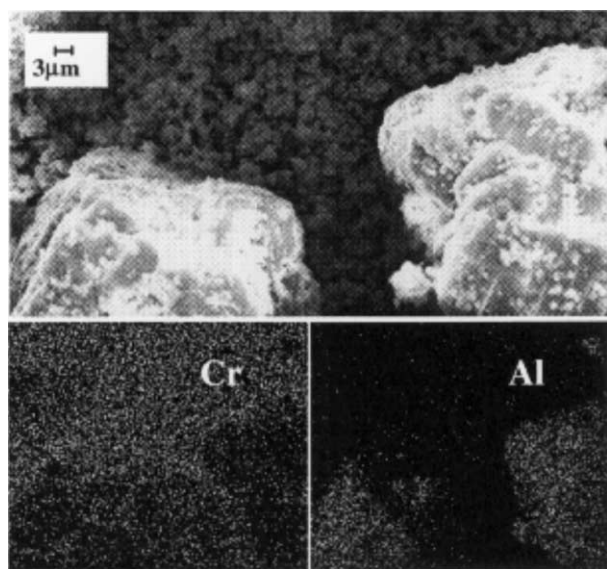


Fig. 5. Micrograph and chromium and aluminium mapping of sample V2IM2 calcined at $1300\text{ }^\circ\text{C}$ for 2 h.

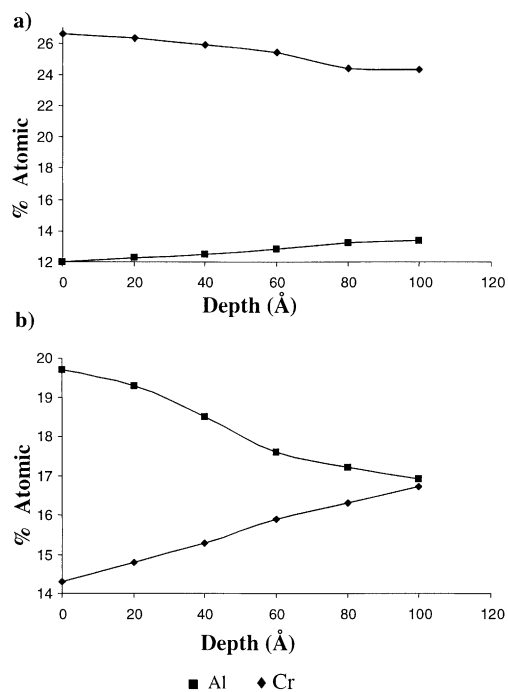


Fig. 7. XPS depth study of the samples calcined at $1300\text{ }^\circ\text{C}$ for 2h: (a) V2IM2; (b) V2LM2.

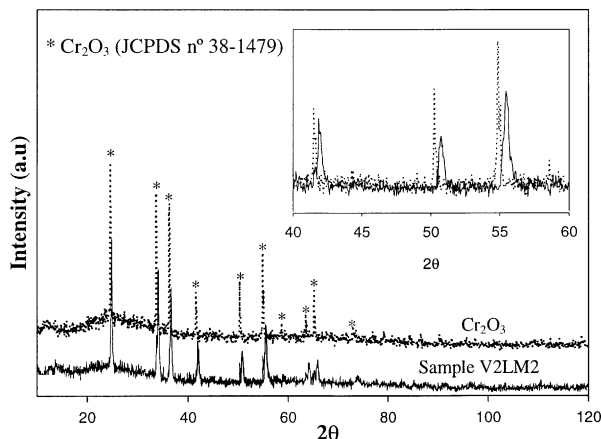


Fig. 8. XRD of sample V2LM2 at 1300 °C and of precursor Cr₂O₃.

indicates formation of a substitutional solid solution in which Al(III) ions replace Cr(III) ions in the Cr₂O₃ network, whose difference in radius in octahedral coordination (67.5 and 75.5 pm, respectively)¹⁶ causes this shift. These results are shown in Fig. 8. In the case of V2IM2, these shifts are not detected, and in accordance with the XPS and SEM findings, this could indicate formation of a very extensive non-solid solution.

4. Conclusions

- Using H₃BO₃ as a mineraliser enables synthesising a green pigment with Cr₂O₃ as chromium precursor and avoiding the use of Cr(VI) compounds. Resulting pigment chromatic co-ordinates (sample V2IM calcined at 1300 °C/2 h) are better than to those of a STD pigment, with lower Cr(VI) contents in the washing waters than the sample without a mineraliser.
- The use of industrial grade reagents improves pigment chromatic co-ordinates, but their use in pigment production has a greater environmental impact compared with that of a sample prepared under the same conditions using reagents of greater purity.
- The difference in behaviour of samples V2IM2 and V2LM2 is to be attributed to the larger particle size of industrial grade Al₂O₃, which notably affects solid-state reactivity.
- In all the samples tested by XPS, the chromium oxidation state was found to be III.
- SEM and XPS analysis indicate that a more extensive solid solution forms with CP grade reagents than with industrial grade reagents. This indicates that the colouring of the pigment synthesised with CP grade reagents is contributed by the solid solution, while colouring is due to Cr₂O₃ with the industrial grade reagents.

- The study has enabled producing a more environmentally friendly green pigment, with good chromatic quality, in which the chromium content has been reduced.

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