# ENVIRONMENTAL PROBLEM OF CHROMIUM-CONTAINING CERAMIC PIGMENTS: OPTIMISATION OF THEIR SYNTHESIS

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## INTRODUCTION

The industrial synthesis of ceramic pigments is carried out by the traditional method and involves washing the pigments before their addition to the glaze. The problems that such processing entails are high energy costs due to the high temperatures, the use of mineralisers that make the starting raw materials more expensive, air and waste water pollution owing to removal of toxic elements, as well as problems of homogeneity and reproducibilidad in pigmenting power.

Chromium is a widely used element in ceramic pigment production, but depending on synthesis conditions, it can be found in different states of oxidation and these generate different properties, stability and coloration.

It is unclear which oxidation state is responsible for 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.

Cr can appear in oxidation states II to VI. The two most frequent oxidation states Cr (III) and Cr(VI) are inter-convertible, with the conversion direction fundamentally depending on medium pH, presence of aerobic and anaerobic conditions, and temperature.

Trivalent chromium, as found in nature, it is not hazardous for living beings; it is a mineral that is found in abundance in the products of the earth, such as fruit, vegetables, milk products, meat and, to a smaller extent, beer and wine. As a trace element, it is an essential component.

In contrast, Cr(VI) is taken into our bodies through the respiratory system, water or food (due to irrigation with polluted water), and can cause acute gastroenteritis, acute hepatitis, allergic dermatitis, chronic laryngitis, gastroduodenal ulcer, chronic conjunctivitis, chronic rhinopharyngitis, perforation of the nasal septum and lung cancer.

The various hexavalent chromium compounds represent the greatest threat, especially due to their genetic effects on crossing the placenta and causing mutations.

Thus, a factor to be kept in mind is the handling of Cr(VI) precursors by workers. The Spanish National Institute of Occupational Health and Safety recommends that the chromium (VI) compound quantity handled should not exceed 1 microgram/$m^3$ during 10 working hours a day.

The quantities of chromium found in the environment mainly come from industrial emissions. Natural emissions into the atmosphere are estimated at some 58,000 tons a year, while those of industrial origin approach 100,000 tons a year.

Chromates remain stable for up to 50 years and are even able to cross viscous soils on migrating to underground strata. Thus, hexavalent chromium can cause irreversible damage to the health of animals and man, as well as to plant life, water, earth and air[1-7].

The present work studied the green pigmenting systems of chromium-alumina and chromium pink-tin. The former possesses a structure based on the corundum network, in which the oxide ions are packed in a compact hexagonal way with 2/3 of the octahedral positions occupied by chromium. Given the similarity of sizes and coordination, Cr(III) can easily be incorporated in the structure substituting Al(III) and forming $Al_{2-x}Cr_xO_3$ solid solutions in the whole range of compositions, but their formation will depend on calcination conditions, as well as on the precursors and mineralisers used[8, 11].

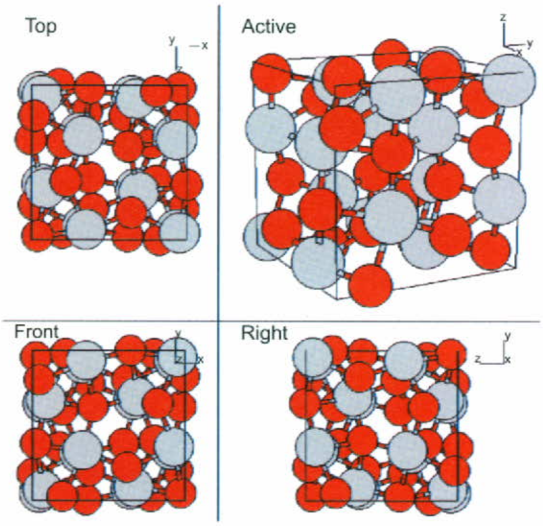

*Figure 1. Corundum structure.*

The second of the above has a structure based on the malayaite network $CaSnSiO_4$, which crystallises in a monoclinic structure. The $SiO_4$ tetrahedrons are linked by tin atoms, which are in turn octahedrally co-ordinated by oxide ions. Depending on formation conditions, the chromium ion can enter the structure substituting Sn[8, 9, 11].

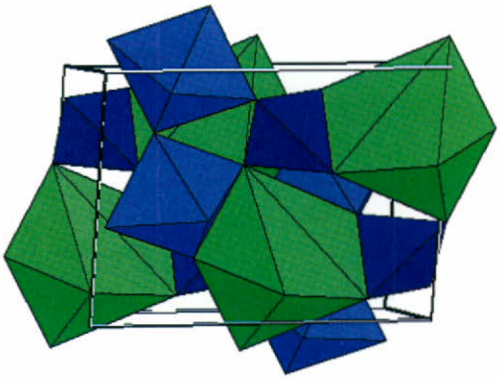

*Figure 2. Malayaite network.*

Both the green chromium-alumina pigment and the chromium pink-tin have been synthesised by different methods[12]. In these a Cr(VI) compound is used as a precursor, which considering the problems that it poses, will not be an appropriate precursor for ceramic synthesis. Moreover, these compounds present the disadvantage that the washing waters will contain appreciable quantities of Cr(VI).

The green chromium-alumina pigment, is synthesised as follows:

- Patent 2,560,338 (Frayne): Sodium dichromate is reduced with sodium thiosulphate, calcining the reduced product.
- Patent 2,659,215 (Pollock): Sodium dichromate is reduced with sodium sulphate, followed by a pH adjustment and subsequent calcination of the resulting product.
- Patent 2,250,789 (Ayers): Anhydrous chromic acid is intimately mixed with a small percentage of an alkaline metal carbonate, subsequently calcining the mixture and washing and drying the resulting product. This process is impracticable because the acid is corrosive and destroys the equipment.
- Patent 4,040,860 (Masmann): Dihydrate sodium dichromate is reduced with chloride or ammonium sulphate and water, heating the resulting mixture for 15 minutes and separating the pigment formed from the salts. This process consumes large quantities of ammonium salts to satisfy the necessary stoichiometry in the reaction.

With regard to the chromium pink-tin pigment, one of the syntheses used, as shown in patent 100,210 (Romania), employs a mixture of $CaCO_3$, $SiO_2$, $SnO_2$ and $K_2Cr_2O_7$ or $(NH_4)_2Cr_2O_7$ as chromium source, although the possibility is mentioned of using $Cr_2O_3$. This is then calcined at 1300-1350°C for 1-4h..

The objective of the present work was the study of these pigmenting structures, which contain chromium as a chromophore element. The specific objectives were:

- elimination of chromium (VI) and halogens as precursors,
- study of different mineralisers as well as their optimisation,

- producing minimum concentrations of chromium (VI) in washing waters,
- raising pigmenting power

## EXPERIMENTAL

### • METHODOLOGY

The study was conducted using the traditional ceramic synthesis method. In this method, after proportioning the precursors, they are mixed and homogenised with acetone in an agate mill. The dispersante is then evaporated and after drying, the samples are calcined in an electric kiln at the studied temperature. To reduce the particle size, after each calcination the samples are milled again in the agate mill with 30% water, previously separating a small proportion for later analysis of the washing waters. After this last milling, the samples are dried at ambient temperature for addition to a ceramic glaze.

In this glaze preparation process a transparent frit is used, to which 3 wt% pigment is added, together with 0.1% carboxymethylcellulose (CMC) and 45% $H_2O$.

These components, are put in an agate mill, mixing and homogenising for 5 minutes, and then applied onto a white body (twice fire). The glazed piece is left to dry in an oven, and after drying is fired in a fast kiln with the following cycle (Figure 3).

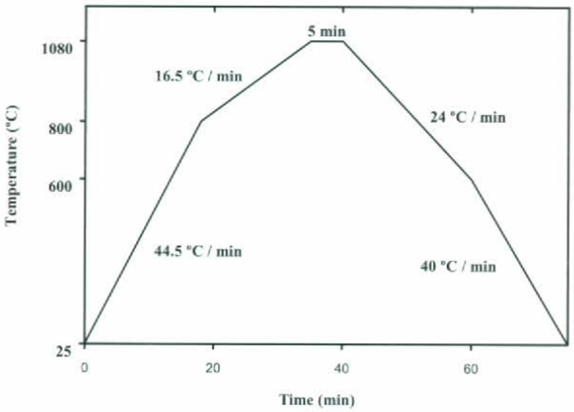

*Figure 3. Glaze firing cycle used.*

### • WORK COMPOSITIONS

The following compositions were prepared in the study:

*Green chromium-alumina pigment*

| | V1 | V2 | V3 |
|---|---|---|---|
| $Cr_2O_3$ | 70% | 65% | 60% |
| $Al_2O_3$ | 30% | 35% | 40% |

*Table I. Compositions studied for the green chromium-alumina pigment.*

A preliminary study was conducted on the 70%-30% composition to determine and optimise the mineraliser and the raw materials used.

In the study of the mineraliser, different classes of mineralisers were tested, which facilitate greater reactivity in the development of the structure and incorporation of the chromophore element, to segregate the smallest quantity of Cr(VI) into the washing waters.

*Chromium-tin pigment*

A sole composition was studied in this pigment: $CaCr_{0.04}Sn_{0.97}SiO_5$. This composition was selected after various preceding studies[15-19].

• CHARACTERISATION

♦ The quantity of Cr(VI) in the washing waters was determined by colorimetry, using as reagents:

- $H_2SO_4$
- Ethyl alcohol
- Diphenylcarbazide
- $K_2CrO_4$
- $HNO_3$

The solutions needed for establishing the calibration curve were:

1. $HNO_3$ 0.3M, in $H_2O$
2. $H_2SO_4$ (1/10 v/v), in $H_2O$
3. A solution of $K_2CrO_4$ with $HNO_3$ 0.3M of concentration 0.1 gCr(VI)/L
4. A solution of $K_2CrO_4$ with $HNO_3$ 0.3M of concentration 10 mgCr(VI)/L
5. Diphenylcarbazide (0.2g.), $H_2SO_4$ 1/10 v/v (400 mL), in ethanol, EtOH

The calibration curve was found by mixing the volume proportions given in table II.

| | **blank** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** |
|---|---|---|---|---|---|---|---|---|---|---|
| **Sol.4** | 0 | 0.25 | 0.5 | 0.75 | 1 | 2.5 | 5 | 7.5 | 10 | 25 |
| **Sol.5** | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| **Sol.1** | Gauging to 50 mL | | | | | | | | | |
| **ppm Cr** | 0 | 0.05 | 0.10 | 0.15 | 0.20 | 0.50 | 1.00 | 1.50 | 2.00 | 5.00 |

*Table II. Calibration curve*

It is necessary to keep in mind that before measuring absorbancy, 2 ml of solution 5 was added to 25 mL of each reference solution, allowing these to rest for 10 minutes.

The absorbancy measurement was carried out on a Perkin Elmer UV/VIS/NIR Lambda 19 spectrophotometer. The results obtained for the 540 nm wavelength, which corresponds to the maximum absorption of the complex that the Cr(VI) forms with diphenylcarbazide were:

| | Cr(VI) ppm | $^{a}A_{mean} \pm S_{n-1}$ |
|---|---|---|
| BLANK | 0 | 0.00006 ± 0.00005 |
| 1 | 0.05 | 0.03470 ± 0.00012 |
| 2 | 0.10 | 0.07280 ± 0.00030 |
| 3 | 0.15 | 0.13520 ± 0.00008 |
| 4 | 0.20 | 0.14560 ± 0.00020 |
| 5 | 0.50 | 0.35390 ± 0.00030 |
| 6 | 1.00 | 0.65026 ± 0.00017 |
| 7 | 1.50 | 0.83526 ± 0.00015 |
| 8 | 2.00 | 1.21690 ± 0.00050 |
| 9 | 5.00 | 2.19440 ± 0.00130 |

[a] $S_{n-1}$ is the standard deviation of n-1 measurements where n= 6.

*Table III. Absorbancy measurement for calibration.*

With the absorbancy results of the prepared references, a linear fit was made, obtaining the equation of a straight line, in which the datum was discarded for 5 ppm of Cr(VI), because $S_{n-1}$ was high (at high concentrations the deviation is larger). The equation of the straight line found was:

$$A = 0.0249 + 0.5855^{*}[Cr(VI)] \qquad r^2 = 0.997 \qquad [Ec.\ 1]$$

Next, 0.3 g pigment was washed with 30 mL $HNO_3$ 0.3M, collecting the mother liquors and gauging with $HNO_3$ 0.3M to 50 ml. The absorbancy measurement was made, and substituted in the equation of the straight line (A), giving the Cr(VI) concentration in the washing waters, taking into account the dilutions made.

◆ Determination of Cr(VI) in the washing waters by atomic absorption[15].

Atomic absorption (AA) spectroscopy uses light absorption to measure atom concentration in the gaseous phase. Since most of the samples are solid or liquid, the atoms or ions of the analytes need to be flame vaporised or vaporised in a graphite kiln. The atoms absorb visible or ultraviolet light that causes transitions at higher energy levels. The analyte concentration is determined by the absorption quantity. The concentration measurements are generally made on the basis of a calibration curve, after having calibrated the apparatus with standards of known concentration.

◆ Determination of the chromatic co-ordinates by colorimetry[13, 14].

Colorimetry serves to characterise a colour and allow identification. The system adopted by the American ASTM, which is generally used in measuring ceramic colours, is the spatial representation of the values: L*, a* and b* of the CIElab method.

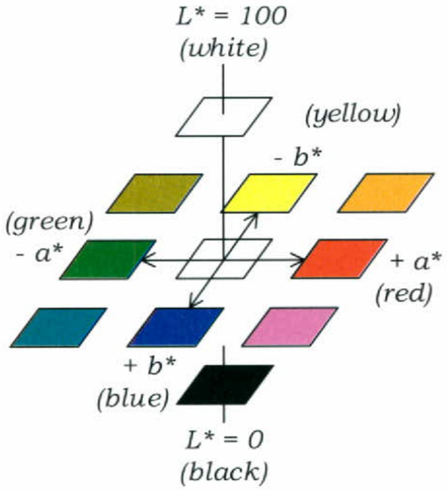

*Figure 4. Spatial representation of the values L*, a* and b*.*

The value of a* indicates the quantity of red (+a*) or green (- a*), while that of b* represents the yellow (+b *) or blue content (- b *). In no case does the numerical value provide a degree of colour saturation. The brightness of the colour is indicated on the L* axis and can range from 0 (black) to 100 (white).

◆ Structural characterisation was done by X-ray diffraction (XRD) and microstructural characterisation by scanning electron microscopy (SEM)[13].

- In this study the XRD data enabling the development of the crystalline phases to be monitored was obtained by the powder method with a Siemens model D5000 diffractometer, fitted with a copper anticathode, nickel filter and graphite monochromator. Measurements were made at a voltage of 40 kV and intensity of 20 mA, in the range 20° to 70° ($2\theta$), 0.05°/s goniometer speed and 1s step count collection time (time constant). Slits of 2.2 and 0.2 mm. were used.

The most important use of the powder method is in the qualitative identification of crystalline phases and the determination of parameters and cell symmetry. Other applications are determination and refining of crystalline structures, the study of the degree of crystallinity or the determination of the size and form of coherent domains.

The powder method possesses certain characteristics that make it one of the most widely used methods at present. These characteristics include ease of sample preparation, performance in a single experiment of the whole diffraction register and accurate determination of lattice spacings (h k l).

- In materials science, detailed knowledge of the physical nature and chemical composition of the solid surfaces on a submicrometer scale is fundamental. For this, microstructural characterisation was performed by SEM with a Leica, Leo 440, instrument. The working conditions for the observation of sample microstructure were as follows: acceleration voltage = 20 kV, probe intensity = 150-500 pA. The samples were deposited as very fine powder in an aluminium sample holder and covered with a fine graphite sheet. Subsequently, a stream of compressed air was injected to remove non-adhered particles and possible impurities stemming from exposure to the ambient, in order to avoid problems with the microscope's vacuum system and minimise interpretation errors.

## RESULTS AND DISCUSSION

### Green chromium-alumina pigment

*Preliminary study*

The samples prepared according to Table I were established in a preliminary study to determine and optimise the mineraliser and raw materials that minimise the chromium content in the washing waters and enable colour development comparable to that of the reference, for which different mineralisers were tested.

$Cr_2O_3$ and $Al_2O_3$ (laboratory reagents) were used as precursors in the proportion 70%-30%, which corresponds to sample V1. This proportion was selected for the preliminary study because of its larger $Cr_2O_3$ content, which enabled observing the effectiveness of the mineraliser on washing water Cr(VI) content. The study was carried out with 4 mineralisers, M1, M2, M3 and a mixture of M2-M3. The range of mineraliser addition was from 0.5-10%. Table IV details the references of the prepared samples and tested mineralisers.

| | V1/M1 | V1/M2 | V1/M3 | V1/M2+3 |
|---|---|---|---|---|
| **$Cr_2O_3$** | 70% | 70% | 70% | 70% |
| **$Al_2O_3$** | 30% | 30% | 30% | 30% |
| **Mineraliser** | M1 | M2 | M3 | M2+3 |

*Table IV. Study of the mineralisers.*

The results found for Cr(VI) in the washing waters for the various samples are listed in Table V:

| SAMPLES | mg Cr/g pigment |
|---|---|
| **V1/M1** | 0.050 |
| **V1/M2** | 0.035 |
| **V1/M3** | 1.988 |
| **V1/M2+3** | 0.041 |
| **REF.1*** | 0.054 |

*Note: remember that reference 1 has already been washed in producing it.

*Table V. Cr(VI) content in the washing waters.*

Figure 5 plots the co-ordinates found for each sample. The Cr(VI) content in the washing waters is represented at the same time by the different colour of the points plotted, the dark green colour being for the samples that had the largest Cr(VI) content.

The graph includes 2 other reference samples, REF.2 and REF.3, which were discarded for the comparative study of Cr(VI) content in the washing waters because of their high Cr(VI) segregation to the waters.

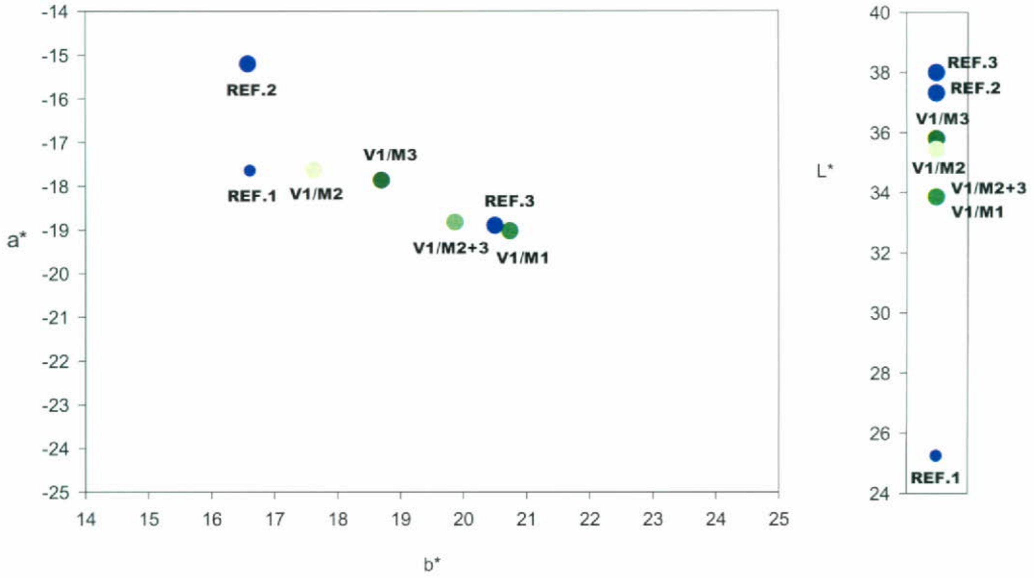

*Figure 5. Study of the mineraliser.*

In view of the findings in Cr(VI) content and chromatic co-ordinates, it was determined that the mineraliser segregating the smallest quantity of Cr(VI) was the one used in sample V1/M2. In the chromatic co-ordinates of the different samples, it cannot be determined which presents a better colour owing to the small difference between them.

The appropriate mineraliser was concluded to be M2, which was the one added to the sample referenced V1/M2.

As indicated previously, after conducting the study of the mineraliser, different raw materials for industrial use were tested. These were $Al_2O_3$-1, $Al_2O_3$-2, $Cr_2O_3$-1, $Cr_2O_3$-2 and $Cr_2O_3$-3. The $Cr_2O_3$-$Al_2O_3$ proportion was 70%-30% by weight, the same as the quantity studied to find the most appropriate mineraliser. All the samples prepared contained a certain proportion of M2. The references of the studied compositions are given in Table VI.

| | **$Cr_2O_3$-1** | **$Cr_2O_3$-2** | **$Cr_2O_3$-3** |
|---|---|---|---|
| **$Al_2O_3$-1** | V1/M2/1 | V1/M2/3 | V1/M2/5 |
| **$Al_2O_3$-2** | V1/M2/2 | V1/M2/4 | V1/M2/6 |

*Table VI. Sample references.*

The calcined samples were washed according to the conditions indicated above. The Cr(VI) contents in the washing waters are detailed in Table VII:

| SAMPLES | mg Cr/g pigment |
|---|---|
| V1/M2/1 | 0.098 |
| V1/M2/2 | 0.119 |
| V1/M2/3 | 0.065 |
| V1/M2/4 | 0.083 |
| V1/M2/5 | 0.355 |
| V1/M2/6 | 0.361 |
| REF.1* | 0.054 |

*Note: remember that reference 1 has already been washed in producing it.

*Table VII. Cr(VI) content in the washing waters.*

As in Figure 5, the chromatic co-ordinates and Cr(VI) contents are plotted in Figure 6.

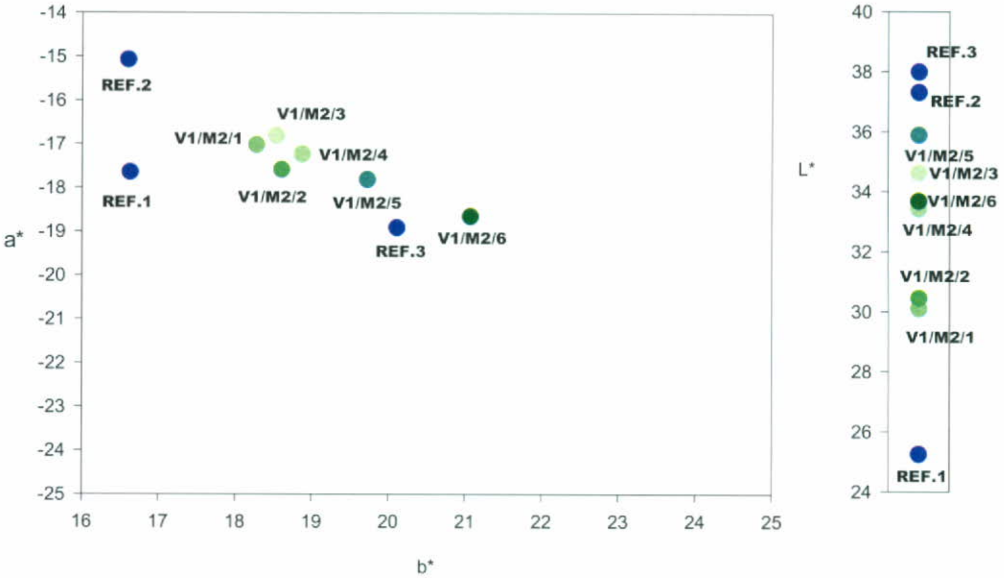

*Figure 6. Study of the raw materials.*

Following the same procedure as above, it was observed that sample V1/M2/1 presented the closest values to those of reference samples 1 (considered as the reference that presented the best chromatic co-ordinates and segregated the least quantity of Cr(VI) in the washing waters). In the selection of the raw material, the economic factor is of great influence, so that it was necessary not only to keep in mind the quantity of Cr(VI) in the washing waters and the chromatic co-ordinates, but also the raw material cost. Therefore, in the present study, the use of the $Cr_2O_3$-2 (of high cost) was practically discarded, despite observing minimum concentrations of Cr(VI) and good chromatic co-ordinates. $Cr_2O_3$-1 was chosen then, which presented low concentrations of Cr(VI), a better value in the chromatic co-ordinates and lower cost, specifically sample V1/M2/1.

It is to be noted that the chromium content in the washing waters increases considerably with the use of industrial raw materials compared with laboratory reagents, as can be observed on comparing the findings for samples V1/M2/1 (reagent for industrial use) and V1/M2 (laboratory analytical reagent).

After these preliminary studies the conclusion could be drawn that using M2 as a mineraliser and $Cr_2O_3$-1 and $Al_2O_3$-1 as Cr and Al precursors led to better colouring results. These reagents were therefore chosen for the study of the different compositions indicated in Table I.

*Study of the suitable precursor quantities*

Finally, the study proposed in Table I was carried out. The results obtained for the chromatic co-ordinates and analysis of the washing waters led to the conclusion that the proportion 65%-35% presented a smaller Cr(VI) content in the washing waters than the reference pigment, while their chromatic co-ordinates were comparable.

| SAMPLES | mg Cr/g pigment |
|---|---|
| V1/M2/1 | 0.098 |
| V2/M2/1 | 0.043 |
| V3/M2/1 | 0.042 |
| REF.1* | 0.054 |

*Note: remember that reference 1 has already been washed in producing it.

*Table VIII. Cr(VI) content in washing waters.*

As in Figure 5, the chromatic co-ordinates and Cr(VI) contents are plotted in Figure 7.

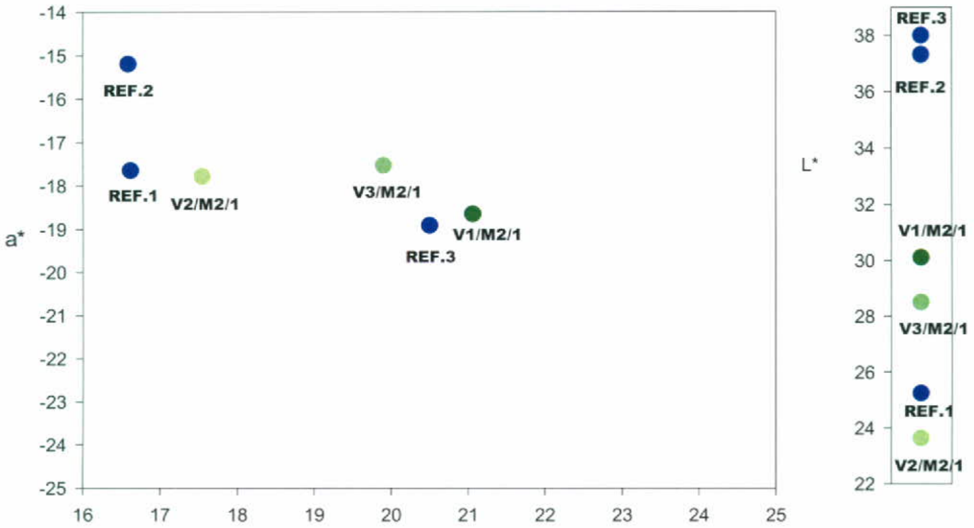

*Figure 7. Study of the optimum precursor proportion.*

With a view to comparing the analyses of Cr(VI) by absorption, with those obtained by flame atomic absorption, an a priori more accurate technique, the sample was analysed which presented the best characteristics by this technique. The results coincided with those found previously, i.e., the sample with the best chromatic co-ordinates and smallest Cr(VI) content in the washing waters was V2/M2/1.

| SAMPLES | mg Cr/g pigment |
|---|---|
| V2/M2/1 | 0.040 |

*Table IX. Cr(VI) content in the washing waters.*

Since sample V2/M2/1 presented interesting characteristic, it was characterised by XRD (Figure 8) in order to study the nature of this pigment. The results indicated that, under the working conditions involved, it formed a single $Cr_2O_3$ phase, suggesting that it could be a Cr-Al solid solution, or that the $Al_2O_3$ was present as an amorphous phase or with very small particle size.

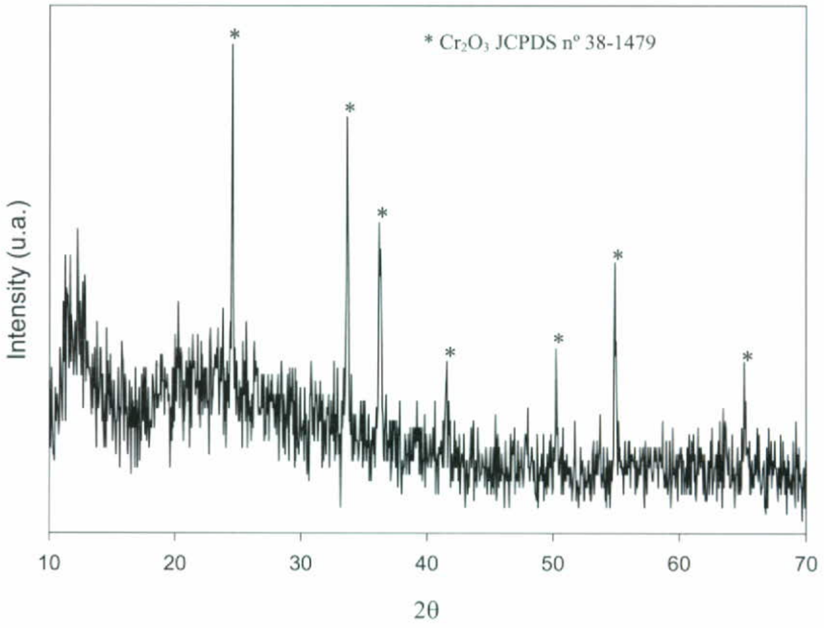

*Figure 8. XRD of calcined sample V2/M2/1.*

To corroborate these results, sample V2/M2/1 was characterised by SEM and semi-quantitative analyses were performed by energy-dispersive X-ray analysis (EDAX). The results indicated, as Figure 10 shows, that there are two classes of solid solution, besides free $Cr_2O_3$ and $Al_2O_3$. It can also be observed that under these working conditions, there is a maximum transfer ratio of 65%-35%, which explains why there is no improvement in the chromatic co-ordinates on increasing the $Cr_2O_3$ content.

According to the SEM results, the mechanism that seems to take place is diffusion of $Al_2O_3$ or $Cr_2O_3$ respectively on $Cr_2O_3$ and $Al_2O_3$ particles, besides the existence of free $Cr_2O_3$ and $Al_2O_3$ as observed in Figure 9. In a previous study carried out by Agustín Escardino, Antonio Barba and Sergio Mestre for the pigment Fe-Cr, a quite similar mechanism was obtained to the one set out here for the green chromium-alumina pigment[19].

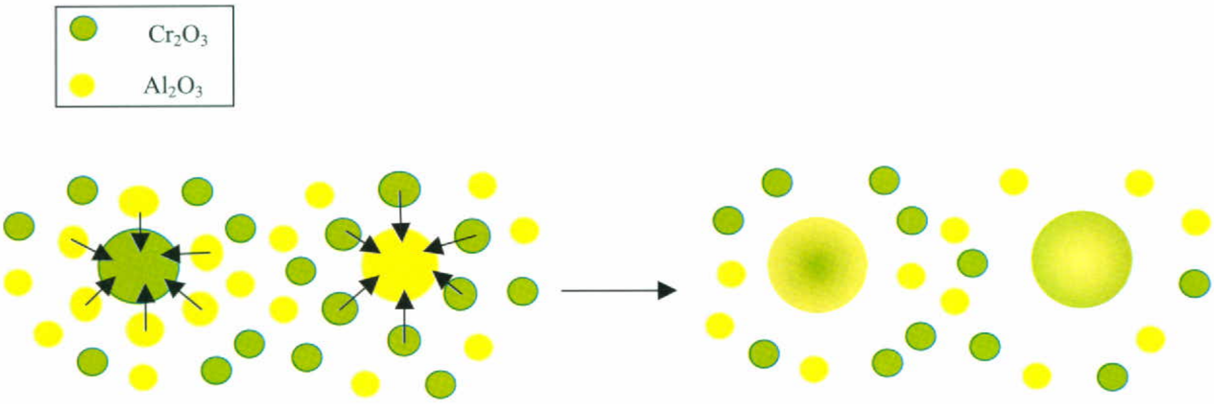

*Figure 9. Chromium-alumina pigment reaction mechanism.*

With a view to explaining why a larger quantity of Cr(VI) is segregated in the washing waters by the other samples, the micrographs of sample V2/M2/1 (sample with smallest Cr(VI) content in the washing waters) and V1/M2/1 (sample with largest Cr(VI) content in the washing waters) were compared before and after washing with water (Figures 10-13). It can be observed that the free Cr content is larger in V1/M2/1, which explains the increase in Cr(VI) in the washing waters.

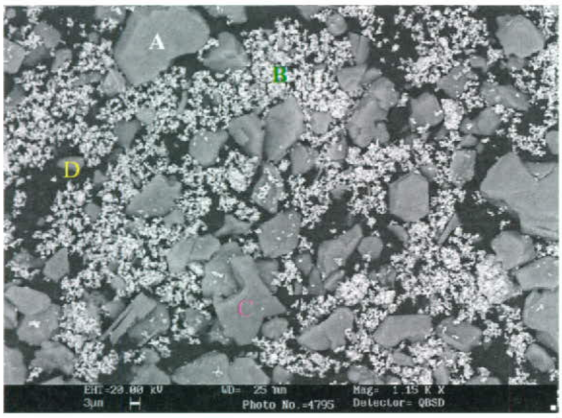

*Figure 10. SEM of calcined V2/M2/1 without washing.*

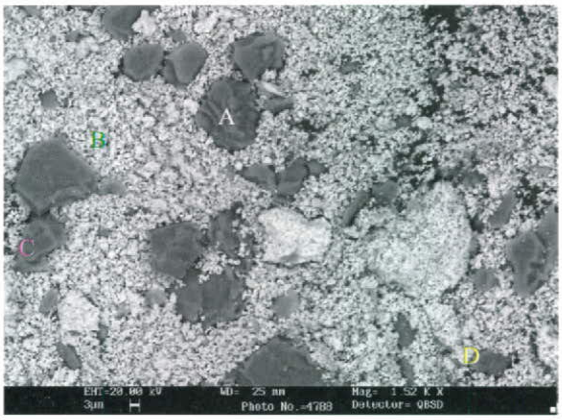

*Figure 11. SEM of calcined V2/M2/1 without washing.*

A → Solid Sol.: 65% $Cr_20_3$ / 35% $Al_20_3$.
B → Free Cr: 95% $Cr_20_3$ / 5% $Al_20_3$.
C → Solid Sol.: 35% $Cr_20_3$ / 65% $Al_20_3$.
D → Free Al: 5% $Cr_20_3$ / 95% $Al_20_3$.

A → Solid Sol: 65% $Cr_20_3$ / 35% $Al_20_3$.
B → Free Cr: 95% $Cr_20_3$ / 5% $Al_20_3$.
C → Solid Sol: 35% $Cr_20_3$ / 65% $Al_20_3$.
D → Free Al: 5% $Cr_20_3$ / 95% $Al_20_3$.

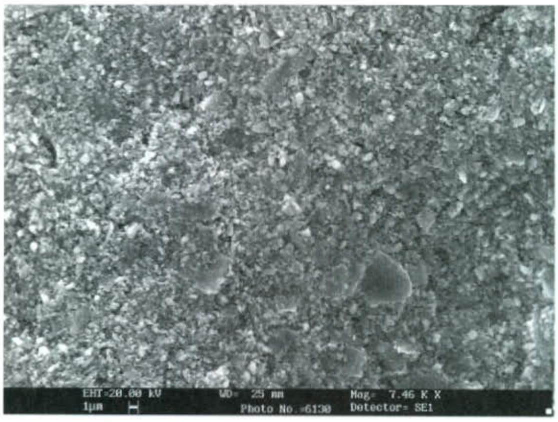

*Figure 12. SEM of V2/M2/1 calcined and washed with $H_2O$.*

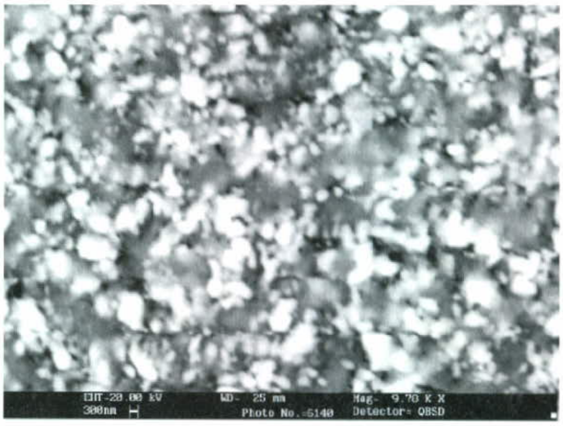

*Figure 13. SEM of V2/M2/1 calcined and washed with $H_2O$.*

### Chromium tin pigment

The pigment was synthesised by the ceramic method using $SnO_2$, $Cr_2O_3$, $SiO_2$ and $CaCO_3$ as precursors, all being of industrial quality. Mineralisers were studied to minimise the Cr(VI) content in the washing waters and to optimise the chromatic co-ordinates.

The references of the samples prepared for composition $CaCr_{0.04}Sn_{0.97}SiO_5$, with different mineralisers are detailed in Table X.

| Samples | M1 | M2 | M3 | M1/M4 |
|---|---|---|---|---|
| E1 | 0.5-10% | - | - | - |
| E2 | - | 0.5-10% | - | - |
| E3 | - | - | 0.5-10% | - |
| E4 | - | - | - | 0.5-10% |

*Table X. Study of mineralisers.*

The samples were prepared by the same methodology as the previous pigment. The chromatic co-ordinates and Cr(VI) contents in the washing waters were then determined.

The results of the Cr(VI) concentration in the washing waters are detailed in Table XI.

| SAMPLES | mg Cr/g pigment |
|---|---|
| E1 | negligible |
| E2 | negligible |
| E3 | negligible |
| REF.1* | 0.051 |

* Note: remember that reference 1 has already been washed in producing it.

*Table XI. Cr(VI) content in washing waters.*

Figure 14 presents the results of the chromatic co-ordinates. Sample E2 is the best one, as it exhibits high values for co-ordinate a*, similar to those of the reference, but with a decrease in the value of co-ordinate b*. The Cr(VI) contents in the washing waters are negligible in all of them.

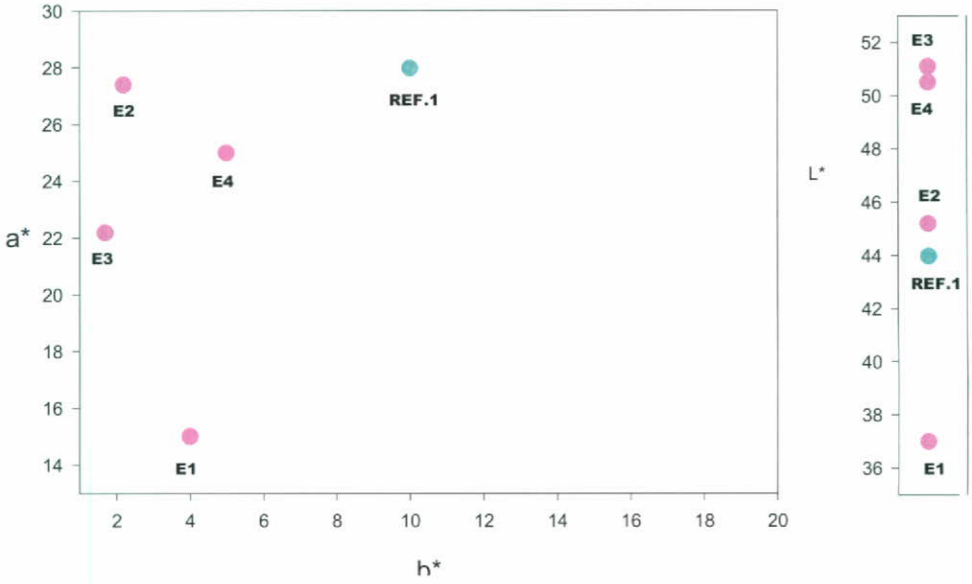

*Figure 14. Chromatic co-ordinates of the chromium-tin pigment.*

The XRD of calcined E2 sample showed peaks corresponding to the malayaite phase together with cassiterite and wollastonite peaks of smaller intensity (Figure 15). These results seem to indicate the formation of solid solution in which Cr replaces Sn in the host network.

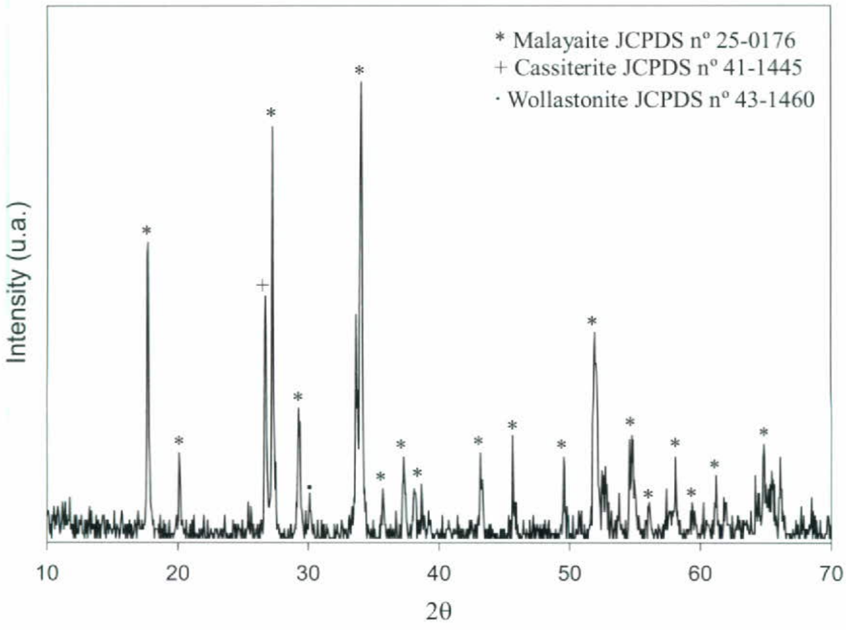

*Figure 15. XRD of calcined sample E2.*

## CONCLUSIONS

- Both the green chromium-alumina and the chromium pink–tin pigment can be produced using Cr(III) as chromium precursor. This fact will have positive repercussions on handling precursors on an industrial level.

- In the two studied pigments, very low Cr(VI) contents are obtained in the washing waters, which implies that their industrial process will have a minimum impact on the polluting quality of waste water.

- The synthesis mechanism in the green chromium-alumina pigment is based on diffusion of $Al_2O_3$ or $Cr_2O_3$ respectively on $Cr_2O_3$ or $Al_2O_3$ particles, as well as the existence of free $Cr_2O_3$ and $Al_2O_3$. In the case of the chromium-tin pigment, a solid solution seems to form in which Cr replaces Sn in the host network.

- The analyses of Cr(VI) in the washing waters indicate negligible quantities of Cr(VI), and smaller than those obtained in commercial pigments of the same nature.

- The values of the chromatic co-ordinates are similar to those of the commercial pigments but with the particularity of negligible quantities of Cr(VI) in the waters and production at lower temperatures.

- It is to be noted that the two pigmenting systems are obtained at considerably lower temperatures than those used in industrial processes.

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