

# CHROMIUM(III) PIGMENTS: USE OF LEATHER WASTES AS ALTERNATIVE STARTING MATERIAL

by

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## ABSTRACT

Chromium containing leather wastes poses potentially significant challenges to the ecosystem when disposed of in landfills or when incinerated in the open. An attempt to recover chromium from such leather wastes so as to reduce the chromium that ends up in the landfill was studied. A method of recovery of the chromium in chromium tanned leathers by controlled closed furnace incineration and by employing the protein matrix as an energy source as well as a template for chromium(III) oxide synthesis is detailed. This method provides the advantage of reducing the chromium residues from the leather industry while producing chromite ore ultimately useful in the preparation of pigmented coatings. The dry pigment obtained was green colored and could be further processed and formulated as a pigmented coating (paint). When the chrome shavings were mixed with iron sulfate and then incinerated, a brown colored paint coating was achieved. The best conditions for zero generation/discharge of hazardous chromium(VI) were determined. The pigments developed were characterized in detail by XRD and SEM-EDAX. Photon correlation spectroscopy measurements indicate that the calcined pigments prior to further size reduction were in the range of 300-400 nm.

## RESUMEN

Residuos de cuero que contengan cromo presentan significantes potenciales retos al ecosistema cuando sean dispuestos en rellenos sanitarios o incinerados al aire libre. Un intento de recuperación del cromo de tales desperdicios de cuero se estudio para así lograr reducir el cromo que termina en tales rellenos. Un método de recuperación de cromo del cuero al cromo por medio de una incineración controlada en un horno cerrado y empleando la misma matriz proteínica como la fuente energética, así como un molde de síntesis del óxido de cromo (III) es detallado. Este método provee la ventaja de reducir los residuos de la industria del cuero mientras produce el mineral de cromita, útil al fin y al cabo, en la preparación de pinturas pigmentadas. El pigmento seco obtenido era verde y podría ser adicionalmente procesado y formulado como un acabado pigmentado (pintura). Cuando las rebajaduras se mezclaron con sulfato de hierro y luego incineradas, se obtuvo una pintura color pardo. Las óptimas condiciones para obtener cero producción/descarga del peligroso cromo (VI) se determinaron. Los pigmentos desarrollados se caracterizaron detalladamente por medio de XRD y SEM-EDAX. Espectroscopía por correlación de fotones determinó que los pigmentos calcinados, antes de moler, tenían un rango [de dimensión] de 300-400 nm.

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## INTRODUCTION

Inorganic pigments are widely used in various applications such as paints, inks, plastics, rubbers, ceramics, enamels and glasses.<sup>1,2</sup> The pigments for coloring ceramics, usually inorganic products composed of metal oxides or compounds formed from the host of metal oxides, must possess thermal and chemical stabilities at high temperature and must be inert to the chemical action of the molten glaze.<sup>3</sup> Chromium pigments form a majority of inorganic pigments with chrome green and chrome yellow dominating the green and yellow range of products.<sup>4</sup> Guignet of Paris patented the process for manufacturing Viridian or transparent oxide of chromium in 1859. This pigment was essentially a Chromium(III) – oxide dihydrate. Its excellent permanence and lack of toxicity replaced all other greens, both ancient and modern. Calcining a mixture of boric acid and potassium bichromate and washing the material thus formed, resulted in Viridian. However, the toxicity of chromium(VI), has led to concerns and the overall production process of this pigment desires radical changes.<sup>5</sup> Thus, serious need arises to search for environmentally friendly and economically viable materials for the replacement of toxic components of chromium pigments. Further, the very use of potassium bichromate, the preparation of which, from chromite ore results in large quantities of chromite ore processing residues (COPR) calls for attention. The large quantities of COPR which ends up as landfills has been predicted as the single cause for the closure of chromite ore processing industries, and this in turn could result in a decrease in production of bichromate salts.<sup>6</sup>

Leather industry is one of the wide spread industries which provides the necessities, such as leather shoes and garments, while utilizing the by-products of the meat industry. Approximately 0.8 million ton solid leather wastes are being generated each year worldwide by the leather industry, with  $\text{Cr}_2\text{O}_3$  content of at least 3.5%.<sup>7</sup> The major quantity of chromium bearing leather waste is the leather shavings (commonly known as the wet blue shavings), which are generated as a part of the leveling process of the leather to meet end use qualities. Current disposal methods include those in landfills, leather boards, filling materials, as a source of gelatin etc.<sup>7</sup> However, the presence of chromium, which can possibly be converted to chromium(VI) during processing have hindered the large scale disposal or usage of this waste material. While the chromium shavings contain 2,200 – 21,000  $\text{mg kg}^{-1}$  chromium, the unfinished leather trimming contain 4,600 – 37,000  $\text{mg kg}^{-1}$  chromium.<sup>7,8</sup> Even though the chromium containing leather shavings is being recycled and reused in many form of products, all those have certain disadvantages like economic viability, and complexity in technical aspects. Some reports on the use of chromium containing leather wastes in chromium pigments are also available.<sup>9-10</sup>

In this work, the synthesis of pigments based on Cr(III) [as its oxide] from chromium bearing wastes has been proposed. The present work proposes a solution to use the leather wastes directly as raw material for chromium pigment. The possible advantages are the use of heat resulting from the burning of organic component (protein) in the energetic balance of the synthesis process of the pigments, and the bound chromium in the leather matrix could be spatially distributed in an uniform manner and the controlled removal of the protein could result in nano sized pigments. The primary focus of this work is to minimize the environmental issues caused by the leather shavings, and the secondary focus is to attempt to bring out Cr(III) colorants or pigments from chrome shavings (without Cr(VI)), leading to alternate source for pigment and reduction of solid waste disposal.

## EXPERIMENTAL

Chromium bearing leather shavings was obtained from a commercial tannery processing raw cow hides to finished leather products. The shavings were separated from the dusts and dusts were sieved through a 1 mm sieve and the resultant material characterized for its chromium content, moisture content and total Kjeldahl nitrogen as per earlier reported procedures.<sup>7</sup> The chromium shavings was then treated at varying temperatures (800-1400°C) for 2 h in a closed furnace, procured from M/s. VB Ceramics, Chennai, India, having an internal volume of 0.22 cu.feet. The ratio of volume of shavings to that of the furnace was 0.06. Variable heating rate of 1 – 7°C/min was employed using a Nippon NC 2438 temperature controller, which enables maintenance of the temperature with a maximum variation of  $\pm 2^\circ\text{C}$ . The gases generated from the shavings result in an air starvation (reductive environment) within the furnace. Subsequently the pigment powder obtained was leached with water for 60 min, flowing at a rate of 5 ml/min, followed by 25 ml of 2 M HCl/gram of pigment, for 60 min. The resultant product was air dried at room temperature and analyzed for the presence of chromium(VI) under varying standard test conditions.<sup>6</sup>

For obtaining brown color, mixing with Fe(II) sulfate [ACS Grade iron(II) sulfate heptahydrate from M/s. Sigma-Aldrich] was performed by immersing the leather shavings in a 0.5 M solution of the mix (10g/100 ml) for 24h, during which time, the entire solution was adsorbed onto the leather fiber. The resultant material was air dried and then treated in the furnace as per above procedure.

The obtained powders were characterized by means of X-ray powder diffraction (XRD) using Ni filtered Cu K $\alpha$  radiation with a Philips X'pert Pro diffractometer. Morphological analysis was performed on the samples directly placed on a carbon tape adhesive on an iron stub. A Leica Cambridge Stereoscan 440 scanning electron microscope was used for the

analysis. The samples were subjected to EDAX analysis in order to determine the distribution of chromium and iron in it. INCA suite program was used for the analysis.

The diffuse reflectance UV-vis spectra were recorded using a Perkin-Elmer lambda 35 UV-vis spectrophotometer equipped with a Labsphere RSA-PE-20 diffuse reflectance accessory. Barium sulfate was used as a white standard. The principle of operation involved projection of light of a known spectral energy on the pellet of colorant (prepared as 5 mm thick, 10 mm diameter pellets by pneumatic compression in a mould) kept at 90° to the light source and measurement of the intensity of the reflected light using photo detectors. CIE illuminant D65 was used in all the color measurements. The CIELab (1976) color space was used for color measurement<sup>12-14</sup> and the colorimetric values were computed using an Advanced Spectroscopy Software (Perkin-Elmer). Each color in the CIELAB color space has a unique location defined by its Cartesian coordinates with respect to the axes  $L^*$ ,  $a^*$  and  $b^*$  where  $L^*$  is the degree of lightness and covered a range from white (100) to black (0) along a grey scale,  $a^*$  is the degree of redness and greenness, and  $b^*$  is the degree of yellowness and blueness. Chroma is the purity of a color. High chroma colors look rich and full. Low chroma colors look dull and grayish.<sup>14</sup>

Particle size measurements were carried out on a photon correlation spectrometer (PCS) from Malvern Instruments (Zetasizer 3000 HSA) equipped with a digital autocorrelator. The concentration of oxide pigments was set to 0.2 mg/ml for all measurements.

The colorants ground and separated to various sizes were analyzed for their mass tone/hiding power. For this a standard commercial paint composition consisting of a long oil alkyd (linseed oil based), as binder, oleic acid as plasticizer and aluminium stearate as rheological agent was used. A paint formulation consisting of 20 g pigment, 50 g resin, 3 g plasticizer and 0.5 g rheological agent was mixed along with mineral turpentine in a ball mill for 60 min. Formulation thus developed was used for coating. The hiding power was evaluated by coating on an opacity chart (coating board) at a thickness of 150 microns. The CIELAB 1976 method of determination of  $L^*$ ,  $a^*$  and  $b^*$  was employed to determine the hiding power of the colorants by comparison of values when coated on white as against that on a black patch.<sup>15</sup>

## RESULTS AND DISCUSSION

The chromium shavings had a  $\text{Cr}_2\text{O}_3$  content of  $3.06 \pm 0.2\%$  on dry weight basis, with a moisture content of  $15 \pm 2\%$ . The apparent density of the material was  $1.5 \pm 0.1$  g/mL. The  $\text{Cr}_2\text{O}_3$  content of 3.06% on dry weight as observed in this study could be advantageously used for the preparation of the pigment. The high nitrogen content (6.55%), is indicative of the large

protein content available in the matrix. The variation in color coordinates and particle size of the pigment with temperature is presented in Table I. It can be seen that the color tends to shift to black at higher temperature of 1400°C. The particle size and color are more or less similar at temperatures of 1000-1200°C. The shift in color could be related directly to the particle size of the pigment. As the particle size changed, the color of the pigment changes. The aim of the work being to obtain green colored pigments, a temperature of 1200°C was taken as optimal. The amount of chromium(VI) in the pigment after a water/HCl leaching cycle was below 0.02 mg/L in all cases (Table II). This is in concurrence with earlier reports that starved air incineration does not oxidize Cr(III) to Cr(VI). Incineration of leather wastes in the presence of oxygen is expected to generate gases such as  $\text{CO}_2$ ,  $\text{SO}_2$  and  $\text{NO}_2$ . In the absence of additional supply of oxygen, the heat developed inside the furnace, generates an inert atmosphere. The high organic content of the shavings provides for reductive environment, thus preventing Cr(III) from oxidizing to Cr(VI). When the furnace is starved of oxygen, CO is generated rather than  $\text{CO}_2$ .<sup>6</sup> However, for large scale application, the use of scrubbers to remove generated gases is ideal. The advantage of the process is that it does not generate any residues, and the need for landfill sites is completely overcome. While no effort has been made to estimate the available oxygen within the furnace, the fact that the Cr(VI) content was minimal or absent is an indication of an air starved condition.

The variation in color coordinates and the number average diameter with rate of heating (treatment temperature of 1200°C) is presented in Table III. The rate of heating had no profound influence on the chromium(VI) content leached from the pigment. However, the pigment prepared with a heating rate of 1°C/min was black in color in comparison to the green colored pigment obtained with 4 and 7°C/min respectively. This is possibly due to the deposition of carbon

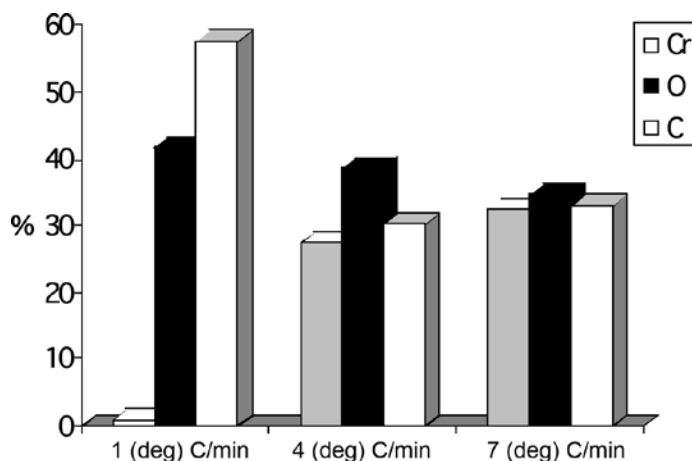


Figure 1. Distribution of chromium, oxygen and carbon content in pigments prepared at varying rate of heating and temperature of 1200°C from EDAX measurements

**TABLE I**  
**CIELAB (1976) color coordinates and hydrodynamic diameter of the chromium pigment (unmixed) obtained at varying temperatures**

Sl.No	Temperature (°C)	L	a	b	Hue Angle	Hydrodynamic Diameter (nm)
1	800	24	-73	54	144	700
2	1000	26	-67	67	135	357
3	1200	23	-74	54	144	324
4	1400	0	0	0	360	64

**TABLE II**  
**Chromium(VI) content in leachate obtained from chromium pigment (unmixed) after various extraction procedures**

Sl.No	Extraction Procedure	Cr(VI) content in leachate (mg/kg) <sup>6</sup>
1	Water (80°C)	0.001
2	NaOH (1 M, 25°C)	0.01
3	Na <sub>2</sub> CO <sub>3</sub> (1M, 25°C)	0.01
4	HCl (25% v/v, 80°C)	0.005

**TABLE III**  
**CIELAB (1976) color coordinates and hydrodynamic diameter of the chromium pigment (unmixed) obtained at various rate of heating**

Sl.No	Rate of heating °C/min	L	a	b	Hue Angle	Hydrodynamic Diameter (nm)
1	1	0	0	0	360	1380
2	4	23	28	43	123	564
3	7	28	27	54	117	397

particles on the chromium oxide formed. The EDAX measurements on this sample showed a large (58%) carbon content, indicating that a lower rate of heating resulted in aggregation of the chromium oxide along with carbon particles (Figure 1). This observation has further been confirmed through particle size measurements, which demonstrate larger sizes at lower rate of heating.

Several applications such as those in external coatings, wood coating and leather employ brown colors. In this work, studies were carried out to generate pigments of brown color through

appropriate doping with Fe(II). The chrome bearing shavings was immersed in a solution of the metal ion, such that the Cr:Fe mole ratio was 1:1. The participating Fe ions, are expected to participate in a redox process, wherein the Cr(VI) would be reduced to Cr(III) and the counter metal ion oxidized. The chromium(VI) leached from the pigment obtained directly from the furnace (without water/HCl leaching) was 0.01 mg/kg. The CIELAB color coordinates were L – 32, a\* - 3, b\* - 20, with a hue of 81°. The hue angle h is defined as starting at +a\* axis and is expressed in degrees. An h value of 90° would indicate yellow color.<sup>11-13</sup> The h value

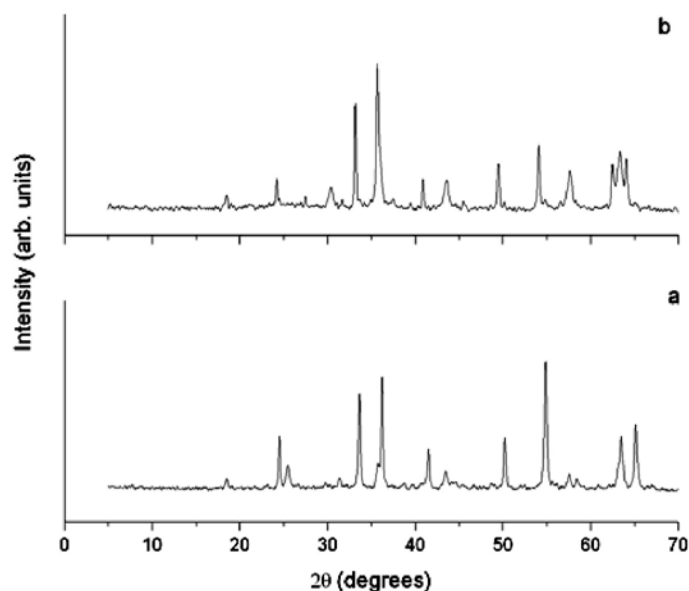


Figure 2. X-ray diffraction patterns of chromium pigment in the (a) absence and (b) presence of iron mixture

of 81 is indicative of a brown color. Larger  $C^*$  value (90) observed in this study, indicates a higher chroma or saturation. Chroma can also be referred to as cleanliness of the color.

The XRD patterns of the colorant oxide in the presence/absence of Fe dopant are given in Figure 2. The XRD pattern of undoped sample (Figure 2a) matched well with that of standard chromium(III) oxide (JSPDS 85-0869). The intense sharp peaks found in the diffraction patterns reveal the crystalline nature of the pigments. The crystallite size was calculated from Debye Scherrer formula,  $D=0.9\lambda/\beta\cos\theta$ , where  $D$  is the crystallite size,  $\lambda$  is the wavelength of the X-ray used,  $\beta$  and  $\theta$  are the half width of X-ray diffraction lines and half diffraction angle of  $2\theta$ .<sup>15</sup> The crystallite size was found to be 25-27 nm for the colorant irrespective of the presence/

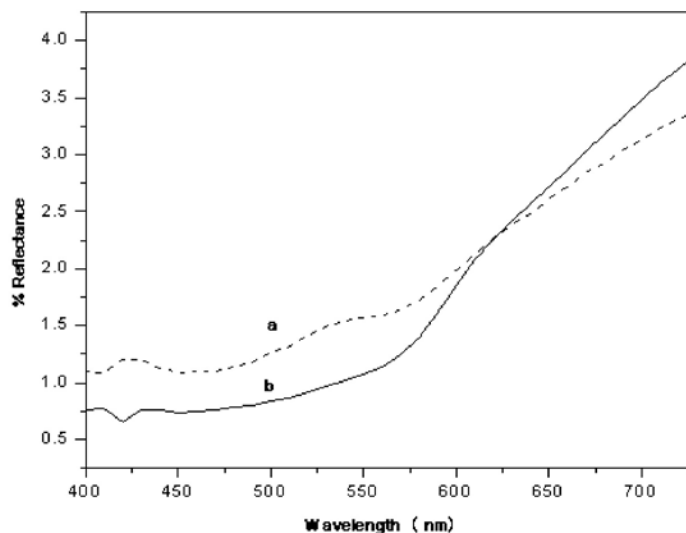


Figure 3. Reflectance spectra for chromium pigment in the (a) absence and (b) presence of iron mixture

absence of dopant. The band gap values are calculated using Kubelka-Munk function which is given by  $K-M = (1-R)^2/2R$  where  $R$  is the reflectance value. A plot between  $K-M$  and wavelength is drawn and the absorption edge is determined from the plot. The value of the wavelength is substituted in the formula  $E \text{ (eV)} = 1236/\text{wavelength}$ .<sup>15</sup> The reflectance spectra of the pigments in the presence and absence of dopant is presented in Figure 3. The bandgap energies ( $E_g$ ) for the doped and undoped sample was found to be 2.16 and 2.33 eV. This change in color from green to brown could be attributed to the change in bandgap energy on account of doping. The scanning electron micrographs for the two pigments are presented in Figure 4 and EDAX spectrum in Figure 5. The SEM-EDAX measurements carried out on the two pigments indicate a uniform distribution.

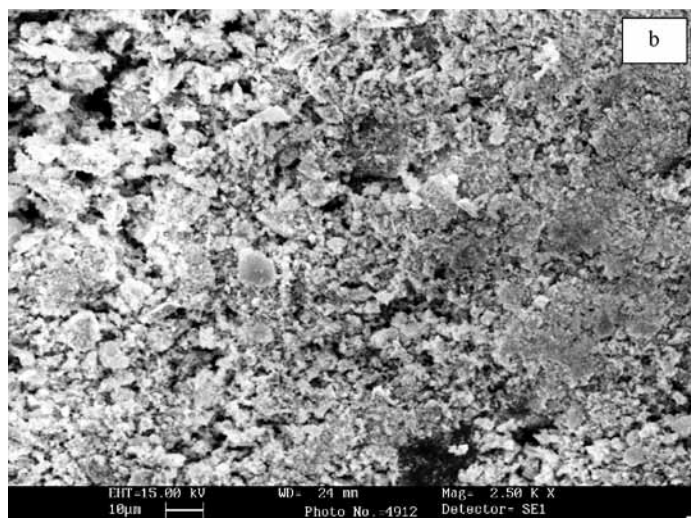
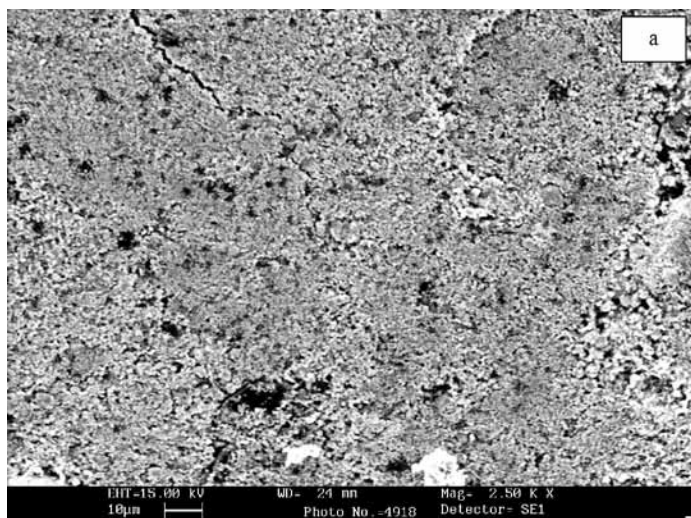


Figure 4. Scanning electron micrographs of the pigment in the (a) absence and (b) presence of iron mixture

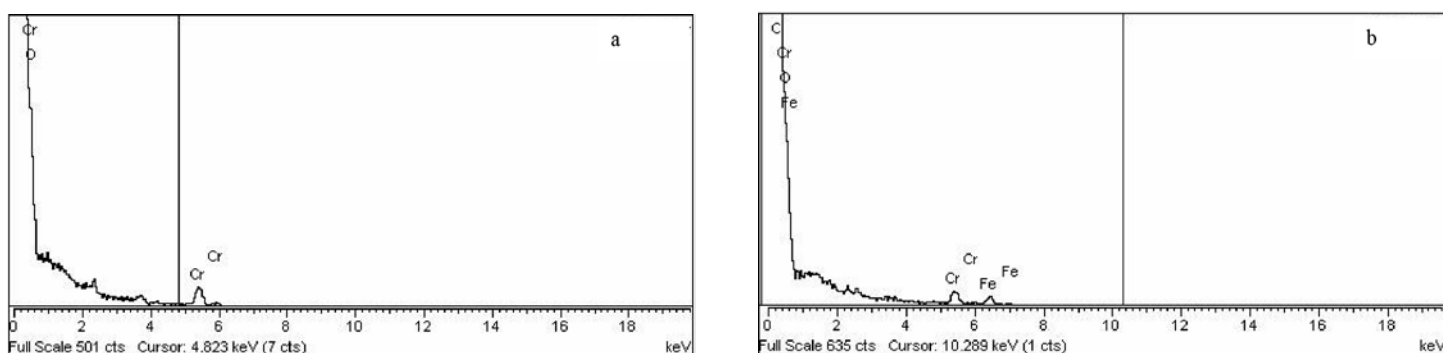


Figure 5. EDAX elemental analysis for Cr and Fe in (a) pigment without doping and (b) with mixture of Fe

**TABLE IV**  
**Color coordinates for the green and brown pigments coated to 150 micron thickness on a coating board**

Color	L	a*	b*	h (deg)	C
On White					
Green	19	-6	12	115	13
Brown	7	10	8	40	13
On Black					
Green	17	-6	9	124	11
Brown	7	10	8	40	13

The two pigments (doped and undoped) were hand ground and the mass tone or hiding power of the pigment was evaluated. Test methods for mass tone have been standardized as per procedures adopted by exterior coating (paint) industries.<sup>15-16</sup> Results are presented in Table IV. A similar value of a\* and b\* on black as against white indicates that the black under layer of the opacity chart was adequately covered by both the pigments.

### CONCLUSION

The use of chromium bearing shavings from the leather industry as raw material for pigments has been demonstrated. The conditions ideal for achieving zero discharge of chromium(VI) have been standardized. The mass tone and covering power of the pigments has been found to be good. A furnace treatment of 1200°C and a rate of heating of 5-7°C/min were found ideal. Doping with Fe(II) not only results in brown colored pigments but also enabled reduction of Cr(VI) through redox processes. The XRD pattern of the undoped pigment matched with that of chromium(III) oxide and the pigments were highly crystalline. The bandgap energy reduced by 0.16 eV on doping.

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