

# Leather pigments: towards a Cleaner Greener Approach

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**Abstract:** Covering of blemishes, mechanical damages etc by way of pigments are essential steps in leather processing. Like other industries, leather industry is also facing the challenge of replacing pigments based on lead, chromium (VI), cadmium etc. This paper reports the synthesis of rare earth based colorants for surface coating applications. Pigments have been well characterized by XRD, SEM, particle size measurements and measurement of hiding power and mass tone. While individual rare earth metal ion based doped colorants are ideal for the fashion world, the conventional leather which is predominantly brown and black require cheaper environment friendly alternatives. Mixed rare earth oxide based colorants and transition metal ion doped pigments developed from chromium shavings are presented as possible alternatives to toxic pigments. Application of mixed rare earth based pigments in leather coloration is discussed in detail.

**Key words:** Rare earth pigments, doping, chromium shavings, hiding power, mass tone

## 1 Introduction

Leather is a unique material which has technological and economic advantages. With increasing consciousness on global environmental security, the leather processing industry is undergoing paradigm shifts from chemical to bioprocessing <sup>[1]</sup>. Unlike other products, leather is both a utility and fashion product. There is an inherent need to retain the feel and visual appearance of leather constant, in spite of radical change in processing. As a fashion product, it is the color of the leather that impresses the buyer more than anything else. Even though, there are pigment free finishes for leather, a reasonable amount of pigment finish, properly applied to any leather, is a benefit to leather in that the color would remain uniform. The pigment would also provide protection against rain, dirt, wear, UV radiation etc, in addition to covering the natural blemishes in the skin. It has been recognized that the cutting value of leather increases on account of pigments as they end up producing even shades.

The list of problems currently affecting leather finishing industry includes the bans on usage of heavy metal ions like chromium, lead, cobalt and nickel in the pigment coat, alkyl tin compounds, alkylphenolethoxylates, N-methylpyrrolidone, formaldehyde and other hazardous crosslinkers in the

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finish formulation [2]. Fortunately the problems associated with the colorants are not specific to the leather industry alone. Plastic and ceramic colorants based on several metal ions are today being phased out [3]. It is with this background that relook into the pigments used for coloring not just leather but several products has become essential.

Pigments have undergone several changes with time. Naturally occurring pigments such as ochres and iron oxides were used in prehistoric times, alongside several pigments from plant bodies. The industrial revolution brought about synthetic pigments, which were classified as organic and inorganic. While organic pigments had good color strength, brightness and an increased solubility in the organic medium used to finish, the inorganic pigments had a greater hiding power, abrasion and UV resistance [4]. Further inorganic pigments resulted in lesser color bleeding than organic pigments. In recent years the environmental and toxicological concerns arising from the use of pigments based on chromium (VI), cadmium, lead, mercury etc has forced pigment industry to look at environmentally benign alternatives. While high performance organic coatings have been employed in several industries, the pigments derived from rare earths have shown promise owing to their characteristic intense color due to charge transfer interactions between a donor and an acceptor with metal ion playing generally the role of an acceptor [5].

The environmental sustainability of leather industry strongly relies on its ability to recover, recycle and reuse its wastes. There is a growing realization in enhancing the atom and energy efficiency of leather processing. With most of utility leather products such as footwear being colored in brown or black, there is a strong possibility in developing brown/black pigments from metal oxides recovered from leather industry itself.

This paper addresses three recent developments in pigment science, viz., developing pigments from rare earth colorants, using mixed rare earth salts (without separating individual rare earth metal ions) for brown pigments and developing colorants from chromium bearing leather wastes. Use of these pigments for coloring leather would also be discussed.

## **2 Experimental**

### ***2.1 Materials***

Cerium carbonate, sodium molybdate, and praseodymium carbonate were obtained from M/s. Sigma Chemicals, USA. Other analytical grade reagents employed in this work were sourced from leading chemical houses in India. Mixed rare earth carbonate employed in this work was sourced from M/s. Indian Rare Earths Limited, Alwaye.

### ***2.2 Metal Oxide Characterization***

Powder X-ray diffraction measurements were performed on a Philips X'pert Pro diffractometer. Morphological analysis was performed using a JEOL JSM 5600LV scanning electron microscope, diffuse

reflectance UV-Vis spectra was 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 white standard. CIELAB (1976) color space was used for color measurements using Advanced Spectroscopy Software. Particle size measurements were carried out on a Zetasizer 3000 HSA. 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  $2\theta$ , respectively. For the sake of simplicity, only the combination of metal ions, temperature and dwell times which gave the best results in terms of spectral features are discussed here.

### ***2.3 Mass tone/hiding power***

Pigments ground and separated to various sizes were analyzed for mass tone/hiding power. For this a standard commercial paint composition consisting of a long oil alkyd dispersing agent and mixed drier was employed. Mineral turpentine was used as the medium. Hiding power was evaluated by coating on an opacity chart at a thickness of 150 micrometer.

### ***2.4 Preparation of Ce-Mo yellow pigments (I)***

Cerium carbonate and sodium molybdate were mixed in the presence of sodium phosphate such that the weight ratio of Ce:Mo:P was 1:0.8:0.6. The mixture was calcined at 900°C for 2 h, employing a heating rate of 5°C/min. The obtained powder was cooled, homogenized and spectral characteristics evaluated.

### ***2.5 Preparation of Ce-Pr-Mo (II) and Ce-Pr-Fe (III) pigments***

Pigments of the above composition were prepared by homogenizing a mixture of cerium carbonate, praseodymium carbonate and sodium molybdate such that the Ce:Pr:Mo was 25:0.2:1. The mixture was then calcined at 1000°C for one hour at a heating rate of 5°C/min. The obtained powder was cooled, homogenized and spectral characteristics evaluated. The change in spectral characteristics when molybdenum was replaced by iron (as iron (II) sulfate) was also evaluated.

### ***2.6 Preparation of mixed rare earth brown (IV) pigments***

High temperature calcination (1300°C/1 hr/5°C/min) of rare earth carbonate sourced from M/s. Indian Rare Earths Limited, Alwaye resulted in rare earth oxide. The oxide was pulverized in a ball mill and particles in the range of 25-45  $\mu\text{m}$  were evaluated for the pigmenting properties. In order to employ them for leather coating applications, they were coated with polyvinyl alcohol in the ratio of 1:0.8 and milled for 8 h. The coated oxide was then mixed with binder and other components of the emulsion and the prepared dispersion evaluated for stability and coating characteristics.

Components of emulsion employed included Pigment 10 parts, 40 parts of soft/medium/hard/micro binder, 5 parts of protein binder, 2.5 parts of wax emulsion, 0.5 parts of ammonia and 42 parts of water. Four cross coats were made and the coated leathers were evaluated for adhesion, light fastness and rub

fastness.

## 2.7 Preparation of doped pigments from chromium bearing shaving dusts













Chromium bearing shaving dusts obtained from a practicing wet blue industry were soaked in solutions of cerium (III) sulfate (*V*), iron (II) sulfate (*VI*), sodium molybdate (*VII*) and manganese sulfate (*VIII*), such that the mole ratio of Cr:metal was 1:1 for a period of 24 hours so as to bring about the chemisorption of the metal ions on the shaving dust. The shaving was subsequently dried at 100°C for 6 h, following which it was calcined at 1200°C for 2h. A control experiment without doping was also carried out at 800 (*IX*), 1000 (*X*), 1200 (*XI*) and 1400°C (*XII*). The obtained pigments were characterized for their color coordinates, hiding/mass tone as well as a leather finish.

## 3 Results and discussion

### 3.1 Color coordinates

The color coordinates and bandgap energies of the pigments developed as a part of this study are tabulated in Table 1.

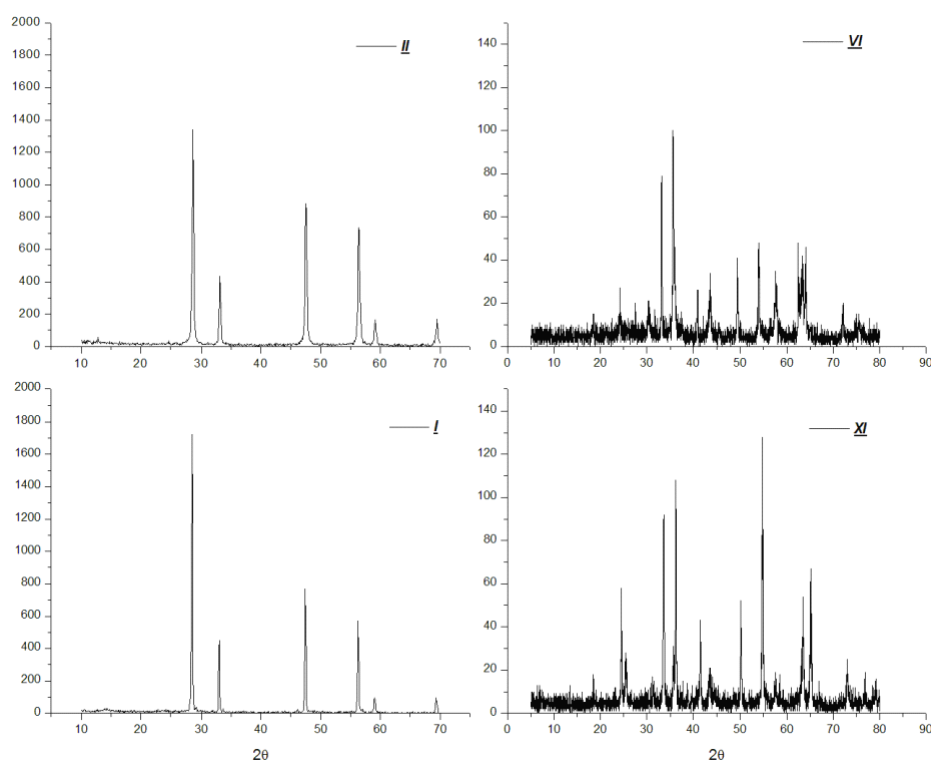
**Tab.1 Color coordinates and bandgap energies for the developed pigments**

Pigment	L	a*	b*	Bandgap energy (eV)	Resultant color
<u><i>I</i></u>	76.1	-0.1	36.9	2.68	
<u><i>II</i></u>	65.7	18.7	31.1	2.24	
<u><i>III</i></u>	66.6	18.1	21.5	2.25	
<u><i>IV</i></u>	63.5	29.1	47.6	-	
<u><i>V</i></u>	81.0	-15.0	33.0	2.30	
<u><i>VI</i></u>	32.0	3.0	20.0	2.26	
<u><i>VII</i></u>	69.0	-18.0	37.0	2.28	
<u><i>VIII</i></u>	25.0	2.0	12.0	2.19	
<u><i>IX</i></u>	34.0	-73	54	2.35	
<u><i>X</i></u>	40.0	-67	67	2.34	
<u><i>XI</i></u>	33.0	-74	54	2.38	
<u><i>XII</i></u>	0	0	0	-	

From the results it can be inferred that the pure rare earth pigments had a higher L value

corresponding to an increased brightness. Cerium and molybdenum doped chromium pigments prepared from leather shavings were bright while those with manganese and iron were darker (lower L values). From 800-1200°C, temperature does not produce a significant change in the color coordinates of the undoped chromium(III) oxide pigment prepared from chromium shavings (However, the resultant Cr(VI) content in the pigment decreased to near zero values at 1200°C. Interestingly at 1400°C, pitch black colored pigment could be synthesized from the undoped shavings. Lower b\* values correspond to a reducing yellowness of the pigments, and this occurred when praseodymium was doped into a Ce-Mo pigment or when Mo was replaced with Fe. When Mo was replaced with Fe, the L and a\* values remained constant with b\* value decreasing by about 10 units, indicating a shift of color from red-yellow to red-blue. The a\* value is a measure of redness or greenness, a positive a\* value is indicative of a red color and a negative a\* value a measure of greenness. For the Ce-Mo system, the a\* was close to zero, indicating that the pigment was yellow. The redness of the pigments increased when Pr was doped into the Ce-Mo system or when Mo was replaced with Pr. For the rare earth oxide pigment (III), the higher a\* and b\* value was indication of the brown color of the pigment. Cerium and molybdenum doped chromium pigment was greenish-yellow, while with Fe and Mn doping the hue shifted toward more brown.

### 3.2 Crystallite, particle size and morphology

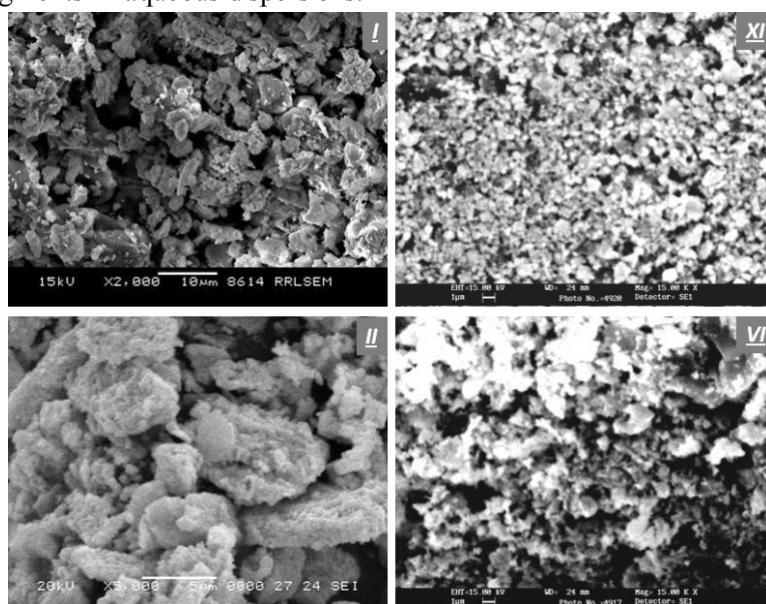


**Fig. 1 Powder XRD patterns for Ce- Mo (I), Ce-Mo-Pr (II), Cr-Fe (III) and Cr<sub>2</sub>O<sub>3</sub> (IV) pigments**

Powder XRD measurements were carried out on Ce-Mo (I) and Ce-Mo-Pr (II) systems as well as on

pigments from chromium shavings (XI) and iron doped shaving (VI). Owing to high temperature processing, all the pigments were highly crystalline (Fig. 1) and in turn would contribute to purer shades with high chroma or cleanliness of color. No significant change in the crystallite size was observed between I and II (36-39 nm) and XI and VI (25-27 nm). Contribution of Pr or Fe in the diffraction pattern was also not detected owing to lower amount of doping.

Dynamic light scattering measurements of water dispersions of the pigments indicated that they were agglomerates of individual crystals. The hydrodynamic diameter of Ce – Mo pigments (I) was found to be 400 nm, while that of Ce – Mo – Pr (II) was found to be 893 nm, the increase in size being due to the contributions from praseodymium ion as well as increased aggregation of the particles. No major change was observed in the case of Cr<sub>2</sub>O<sub>3</sub> and Fe doped Cr<sub>2</sub>O<sub>3</sub> pigments with the particle size being 398 and 423 nm respectively. The morphology of the particles were also analyzed using SEM and were found to be more or less uniform even without any particle size reduction methodologies being adopted (Fig. 2). From the particle size, it could be inferred that the agglomeration of particles need to be prevented for application of the pigments in aqueous dispersions.

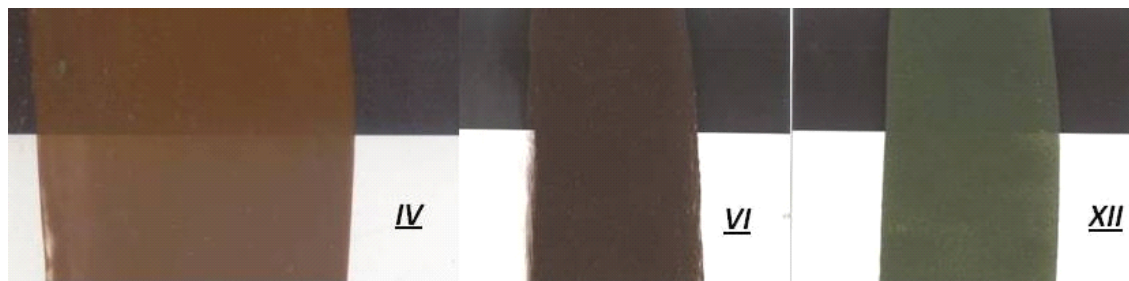


**Fig. 2 Morphology of Ce- Mo (I), Ce-Mo-Pr (II), Cr-Fe (VI) and Cr<sub>2</sub>O<sub>3</sub> (XI) pigments without size reduction process**

**Tab. 2 Mass tone and hiding power of the pigments**

Pigment	Condition	L	a*	b*
<u>II</u>	On White	43.4	25.3	30.04
<u>IV</u>	On Black	40.6	17.3	23.8
<u>VI</u>	On White	7.0	10.0	8.0
<u>VI</u>	On Black	7.0	10.0	8.0

<u>XII</u>	On White	19.0	6.0	12.0
<u>XII</u>	On Black	17.0	6.0	9.0



**Fig. 3 Mass tone and hiding power of Ce- Mo (IV), Ce-Mo-Pr (VI), Cr-Fe (XII) and  $\text{Cr}_2\text{O}_3$  (XI) pigments**

### ***3.3 Mass tone and hiding power***

Mixed rare earth carbonate pigment (IV) as well as those prepared from chromium shavings, viz, undoped (XI) and Fe doped pigments (VI) were hand ground and sieved to obtain particles in the range of 25 – 45  $\mu\text{m}$  and the mass tone or hiding power of the pigments evaluated. Test methods for mass tone have been standardized as per procedures adopted by exterior coating (paint) industries. Results are presented in Table 2. A lower value of  $a^*$  and  $b^*$  on black as against white indicates that the black under layer of the opacity chart was not adequately covered, which in turn means that the ability of the pigment to cover defects or blemishes is poor. This is possibly because of a large number of particles of varying sizes being present in the sample. A better mass tone or covering power could be obtained by screening the particles to uniform size. The stability of the emulsion with time was evaluated visually for different range of particles and it followed the order  $>63 \mu\text{m} < 45\text{-}25 \mu\text{m} < 25 \mu\text{m}$ . The respective shade cards are presented in Fig. 3.

### ***3.4 Mixed rare earth oxide based leather finishes***

Leather pigments need to provide optimal performance not only in solvent based systems but also in waterborne systems which are finding increased usage owing to environmental issues. Compared to other industries, aqueous pigmented coatings are most widely used coatings in leather manufacturing. Pigment concentrates (paste consistency pigment dispersions), various additives and water to dilute are blended together to obtain the desired formulation. Aqueous pigmented coatings are complicated colloidal systems and their stability against coagulation is of paramount importance. By coating the rare earth based oxide pigment with polyvinyl alcohol, the stability of the pigment in water emulsion increased as indicated in an increase in zeta potential values by a magnitude of 20 mV. The influence of binder (soft, medium, hard and micro) on the finish film characteristics is presented in Table 3. The microbinder due to lower size provides for a higher  $b^*$  value and is also more hydrophobic in character (a higher  $\gamma_s^p$  (the vapor-to-water distribution coefficient), measured using a home built goniometer [6], is an indication of higher hydrophobicity). Industrial experts have evaluated the finished leathers as comparable to conventional

leathers.

**Tab. 3 Effect of nature of binder on the finish film characteristics**

Parameter	Soft	Medium	Hard	Micro
Visual Evaluation	3	3	3	3
Adhesion of finish	2/3	2/3	4	2/3
Wet rub fastness	2/3	3	3	2//3
Dry rub fastness	2/3	2/3	3	3
Color				
L	21.3	26.0	20.6	28.7
a*	21.0	21.3	19.0	23.6
b*	29.9	33.4	28.2	41.9
$\gamma_s^P$ (mN/m)	4.0±0.2	3.3±0.1	3.6±0.4	5.6±0.2

#### **4 Conclusions and future perspectives**

Rare earth metal ion based pigments with possibilities of obtaining various hues by way of doping with rare earth and transition metal ions have been demonstrated successfully. These pigments offer wider scope in terms of higher resistance to bleeding and abrasion, in addition to their environmental friendliness. The mixed rare earth oxide based brown pigments as well as iron doped chromium pigments synthesized from chromium shavings offer cheaper, environmentally friendly alternative to toxic brown, green and black pigments. By combining the strengths of rare earth pigments with that of chromium pigments generated from leather wastes cost effective pigment in various hues and shades, with higher chroma or purity can also be developed. Modifications to rare earth pigment chemistry with recent developments in up-conversion rare earth based nanoparticles could pave way to generation of leather coatings which change in color with incident light as well.

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