



## Cool pigments for leather finishing

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### 1.0 Introduction

Modifying the leather finish formulations in such a manner that the customer preferences are met effectively has been one of the major goals of leather researchers. Temperature of leather used, be it the upholstery in the convertibles or the garment worn in tropic conditions is an important comfort parameter modifiable using finish formulations. Leather can reflect or absorb solar energy from UV, visible or infrared regions. Forty-five percent of the total solar energy being in the infrared region, the ability of leather to reflect near infra-red radiations (NIR) determines the comfort factor from leather employed as upholstery or garments. Skin without the melanine and keratin has been reported to have an inherent solar reflective property (1). A significant large number of pigments employed in leather finishing such as carbon black, iron oxide black etc have very low total solar reflectance. This brings in a precarious situation where a material (skin) with inherently high solar reflectance, loses the same on conventional finishing. Further, very few colors used in leather finishing are single pigment dispersions. In order to match a color, more than one pigment is mixed together and the combined pigment is reported to have lower total solar reflectance than the weighted average of individual pigments. Even organic carbon contaminants have been reported to decrease the total solar reflectance of a coating (2).

In addition to the comfort properties, there is also a need to relook into the types of pigments employed in the industry. For instance, several of the conventional inorganic pigments used in several industrial applications contain potentially toxic elements such as cadmium, cobalt, chromium, lead, antimony or selenium (3). Even organic pigments such as copper phthalocyanine, the largest fraction of the organic pigments in the market today is considered to be practically non toxic only due to its low water solubility (4). This brings in a serious need for pigments that are environmentally friendly and economically viable. Low toxicity associated with the lanthanides has provided a niche for this group of elements as ideal replacements for transition metal ion based colorants (5). CeO<sub>2</sub> promotes opacity in ceramic glazes, and praseodymium-zircon color is the best commercial yellow ceramic pigment (6). Similarly, cerium sulfide has substituted the orange and red colors based on the cadmium sulfoselenide pigment used in the ceramic and painting industries (7). The unique optical properties of lanthanides make them useful in a wide range of applications that includes inorganic pigments, tunable lasers, amplifiers for optical communications and organic light-emitting diodes (8-10). It has been suggested that the coloring mechanism of rare earth pigments such as those composed of Y, Mo and Pr is based on the introduction of an additional 4(f1) electron energy level of  $Pi(4+)$  between the valence and conduction bands (11). Such pigments also have high near infra red reflectance (11, 12).

This paper reports the development of blue colorants based on a combination of rare earth metal ions and transition metal ions as cool pigments for potential applications in leather.



## 2.0 Experimental

### 2.1 Materials and methods

**Reagents:** All reagents used in this study were of Analar grade. Cerium chloride and praseodymium carbonate were sourced from M/S Aldrich chemicals, USA while other chemicals were sourced from leading chemical houses in India

### 2.2 Method of preparation

The rare earth metal ions and transition metal ions were taken in appropriate ratios, homogenized using a mortar and pestle and transferred to an alumina crucible. The mixture was calcined at an optimized temperature of 1000°C for 2h at a heating rate of 5°C/minutes. The calcinations was carried out in a small electrically heated, fibre insulated high-temperature furnace with extremely short heating and cooling cycles, which had useful chamber dimensions: app. 150X150X200mm(wxhxd). The chamber volume of the furnace was approximately 4L. The external volume of the furnace was app. 600x600x600mm (wxhxd).

### 2.3 Characterization

The crystalline character and phase purity were determined by means of X-ray diffraction (XRD) using Ni-filtered Cu  $\alpha$  radiation with a Philips Xpert pro diffractometer. The diffuse reflectance UV-vis spectra of the pelletized samples were recorded using a perkin-Elmer Lambda 35 UV-vis spectrophotometer equipped with a labsphere RSA-PE-20 diffuse reflectance accessory. Barium sulphate was used as a white standard. CIE illuminant D65 was used in all the colour measurements. The CIELab (1931) color space was used for color measurement. The colorimetric values were computed using an advanced spectroscopy software. The band gap energy was obtained using the Kubulka-Munk reemission function, which is used as a measure of absorption by the powdered samples. The function K-M is given by  $K-M = (1-R)^2/2R$ , where R is the reflectance. The energy co-ordinates of the point on the low-energy side of the curve at which the linear increase in K-M starts has been taken as the value of the forbidden energy gap of semiconductors[13]. A plot of 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  $E \text{ (eV)} = 1236/\text{Wavelength (nm)}$ .

For the preparation of the pigment formulation, the oxide was pulverized in a ball mill and separated into compositions with >63 microns, 63-45 microns, <45 microns and <25 microns for further studies. Light scattering measurements were carried out at 90° using photon correlation spectroscopy (PCS) on a Malvern Instruments Zetasizer 3000 HSA equipped with a digital autocorrelation for determining the particle size. The non-negative least squares method (NNLS) of correlation and analysis was employed to determine the particle size for an oxide pigment concentration of 0.2 mg/ml. Varian Cary 5E UV-vis-NIR spectrophotometer equipped with a 150mm integrating sphere was used to measure each pigments reflectance in the NIR region. Optical measurements were performed at 5nm intervals over the solar spectrum (350-1200 nm).



## 2.4 Masstone/hiding power of the pigments

The pigments ground and separated to various sizes were analyzed for their mass tone/hiding power. For this the pigment was dispersed in linseed oil. The hiding power was evaluated by coating on an opacity chart at a thickness of 150mm. The CIE LAB 1931 method of determination of L, a and b was employed to determine the hiding power of the pigments by comparison of values when coated on white as against that on a black patch.

## 2.5 Finish formulation for leather

For the preparation of a finish formulation, the pigment particles were mixed with polyvinyl alcohol at the ratio of 1:0.8 and ground in a pulveriser at 5000 RPM for 5 h. The coated particles were then dispersed in standard medium for the preparation of an aqueous finish.

## 3.0 Results and discussion

### 3.1 Pigment preparation

The visual color of the calcined powders Al: Cu: Co: Ce: Pr varies from light blue to darker blue with the variation of praseodymium salts. Red, black green and yellow pigments have also been synthesized by varying the transition metal ions. The synthesized pigments were compared with titanium dioxide as a standard. The hydrodynamic diameter of the blue pigments is given in Table 1.

**Table 1. Particle size distribution of the pigments**

Sample	Composition	Hydrodynamic diameter (nm)	Color
Al:Cu:Co:Ce:Pr	2: 0.2: 0.2: 0.15: 0.05	890.3	Blue
Al:Cu:Co:Ce	2: 0.2: 0.2: 0.15: 0.0	1621.6	Blue
Al:Cu:Co:Ce:Nd	2: 0.2: 0.2: 0.15: 0.05	821.2	Blue
Al:Cu:Co:Ce	2: 0.2: 0.2: 0.2	1224.6	Blue
TiO <sub>2</sub> (commercial)	-	7620.3	White

### 3.2 Vis-NIR spectroscopy

The UV-Vis-NIR reflectance spectra for the blue and white samples are shown in **Figure 1**. It can be observed that the pigments had a reflectance of 70-80% in the wavelength range of 1000-2200nm. A comparison with TiO<sub>2</sub> indicates that these pigments can serve as cool pigments.

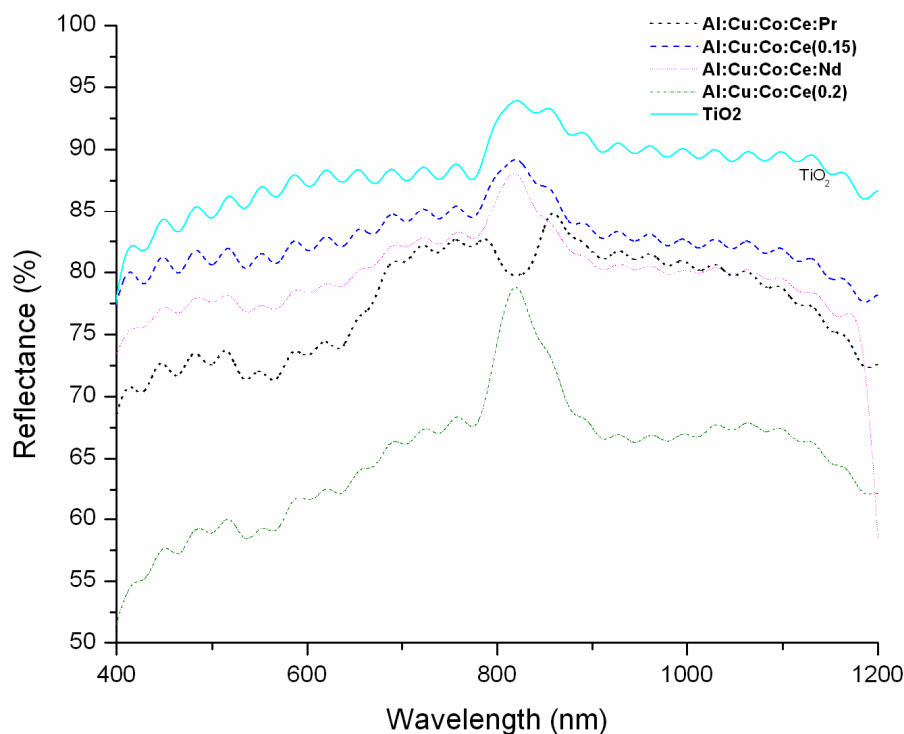


Fig.1 Vis-NIR spectrum of the blue and white pigments

### 3.3 Adjusting the hue of the pigments

The effect of dopant changes the optical properties of the pigment. With neodymium there is an improvement of blue hue of the pigment. The change in color is also evident from the decrease in band gap value as shown in **Table2**.

### 3.4 Color coordinates and analysis of mass tone of the pigments

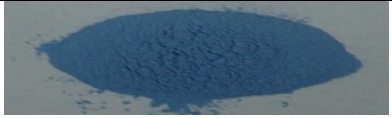



The color coordinates of the pigments are presented in Table 3. When praseodymium is replaced with Neodymium there is an increase in the intensity of blue hue as shown by more negative b value. The developed pigment with a combination of Al: Cu: Co: Ce: Pr (2:0.2:0.2:0.15:0.05) was prepared in bulk quantities of 100g. The pigment was then dispersed into a standard medium employing a ball mill. The paint developed in this way was coated on a board with a checkered, white and black background. The ability of the pigment to cover the black reflected its mass tone or hiding power. Comparisons were made against a titanium dioxide pigment. The color difference has been quantified on the CIELAB-based color difference ( $\Delta E$ ) which is calculated using the following equation.

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

The color difference between the black and white regions was found to be very large indicating that the pigment has poor hiding power or in turn high transparency.



**Table2.Band gap values of the pigments**

Sample	Composition	Band gap (Eg)	Color
Al:Cu:Co:Ce:Pr	2:0.2:0.2:0.15:0.05	2.06	
Al:Cu:Co:Ce	2:0.2:0.2:0.15	2.02	
Al:Cu:Co:Nd	2:0.2:0.2:0.15:0.05	1.94	
Al:Cu:Co:Ce	2:0.2:0.2:0.2	2.05	
TiO <sub>2</sub>		2.07	

**Table. 3: Color coordinates and ΔE values of pigments**

Sample	Composition	Covering power	L	a	b	h	c	ΔE
Al:Cu:Co:Ce:Pr	2:0.2:0.2:0.15:0.05	Black	33.77	-2.82	-3.50	231.15	4.50	26.14
		White	59.33	-	-9.29	219.09	14.73	
				11.43				
Al:Cu:Co:Ce	2:0.2:0.2: <u>0.15</u>	Black	34.87	-1.71	-2.48	235.38	3.01	48.33
		White	83.05	-6.66	1.27	169.16	6.78	
Al:Cu:Co:Ce:Nd	2:0.2:0.2:0.15:0.05	Black	33.37	-2.36	-5.84	248.01	6.29	32.99
		White	65.88	-5.00	-	245.13	11.90	
					10.80			
Al:Cu:Co:Ce	2:0.2:0.2: <u>0.2</u>	Black	36.89	-2.65	-9.48	254.37	9.85	25.32
		White	62.59	-5.10	-9.42	241.57	10.71	
TiO <sub>2</sub>		Black	78.46	-2.47	-3.02	230.73	3.90	20.7
		White	99.10	-1.43	5.27	105.15	5.46	

The inorganic class of NIR reflective pigments being mostly metal oxides with primary applications as camouflage and cool pigments, these pigments predominantly based on rare earth and having IR reflectivity more than 50% are extremely useful as cool pigments. The powder XRD measurements of the samples (data not shown) indicate a crystalline character of the pigments, which also provides sufficient clue to the high reflectance in the NIR region. Leather being a reflective surface, the coating on the leather is expected to be beneficial. Further studies on the cool character of the coated leathers are underway.



## 4.0 Conclusion

It has been possible to utilize the environmentally benign cool pigments generated for leather coating purpose. With a reflectance of over 70% the blue pigments serves as cool pigments for leather coating applications. By appropriate doping of transition metals red, green, yellow, black pigments have also been synthesized in a similar way. The process of formulating the pigment for leather finishing has been optimized with hydrophilic reagents like PVA at a ratio of 1:0.8 to overcome the steric hindrance factors and hence better interaction between pigment and binder, a ball milling time of around 5 h. At this ratio the leather is more hydrophobic in character. The pigment also finds application in covering of surface with low pigment loading, retaining the aesthetics of the grain and improved levelness, excellent physical properties, ageing resistance and miscibility with water.

## 5.0 References

1. Green, A.C., Premature aging of the skin in a Queensland population, *Med. J. Aust.* 155:473-478 (1991).
2. Levinson, R., P. Berdahl, A.A. Berhe, and H. Akbari, Effects of soiling and cleaning on the reflectance and solar heat gain of a light-colored roofing membrane, *Atmos. Environ.* 39:7807-7824 (2005).
3. Sreeram, K.J., R. Srinivasan, J.M. Devi, B.U. Nair, and T. Ramasami, Cerium molybdenum oxides for environmentally benign pigments, *Dyes and Pigments* 75:687-692 (2007).
4. Jo, H.-J., E.-J. Park, K. Cho, E.-H. Kim, and J. Jung, Toxicity identification and reduction of wastewaters from a pigment manufacturing factory, *Chemosphere* 70:949-957 (2008).
5. Garcia, A., M. Llusar, J. Calbo, M.A. Tena, and G. Monros, Low-toxicity red ceramic pigments for porcelainised stoneware from lanthanide-cerianite solid solutions, *Green Chemistry* 3:238-242 (2001).
6. Blosi, M., M. Dondi, S. Albonetti, G. Baldi, A. Barzanti, and C. Zanelli, Microwave-assisted synthesis of Pr-ZrSiO<sub>4</sub>, V-ZrSiO<sub>4</sub> and Cr-YAlO<sub>3</sub> ceramic pigments, *Journal of the European Ceramic Society* 29:2951-2957 (2009).
7. Velleret, G., Red cerium sulfide pigments - new cadmium-free inorganic red pigments for the plastics industry, *Antec 93 : Be in That Number, Vols I-3* 39:13-15 (1993).
8. Eliseeva, S.V., and J.-C.G. Bunzli, Lanthanide luminescence for functional materials and bio-sciences, *Chem Soc Rev* 39:189-227 (2010).
9. Parker, D., Excitement in f block : structure, dynamics and function of nine-coordinate chiral lanthanide complexes in aqueous media, *Chemical Society Reviews* 33:156-165 (2004).
10. Bunzli, J.C.G., and C. Piguet, Taking advantage of luminescent lanthanide ions, *Chemical Society Reviews* 34:1048-1077 (2005).
11. George, G., V.S. Vishnu, and M.L.P. Reddy, The synthesis, characterization and optical properties of silicon and praseodymium doped Y<sub>6</sub>MoO<sub>12</sub> compounds: Environmentally benign inorganic pigments with high NIR reflectance, *Dyes and Pigments* 88:109-115 (2011).
12. Sreeram, K.J., C.P. Aby, B.U. Nair, and T. Ramasami, Colored cool colorants based on rare earth metal ions, *Solar Energy Materials and Solar Cells* 92:1462-1467 (2008).



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