INTRODUCTION

Colourants are characterized [1-3] by their ability to absorb light selectively in the visible region (380-780 nm). Electronic (absorption and reflection) spectra have been used to investigate some corrections between chemical structure and colour of the species. The characteristic parameters of the spectrum, i.e. the positions of absorption bands and their intensity and shape are important factors in the determination and prediction of colour [4] and these parameters are dependent upon the electronic structure and symmetry of the clues. Theoretical problems connected with the nature of colour have been studied extensively, especially in case of the organic dyes.

One of the most important problems in colour technology is how to attain a specified colour using a mixture of colourants [5]. A tristimulus colorimetry is generally employed for colour measurement. The principle of operation involves projection of light of a known spectral energy on the pellet and measurement of the intensity of the reflected light using photo detectors. All the synthesized pigment samples are found to be having colour coordinates and exhibit the colour from pale yellow to orange red. Reflectance spectra of the samples show high reflectance percentage in the 600-800 nm range. Because of the homogeneity of the phase formed the intense colouration the yttrium doped pigments have been found to be superior to cerium doped pigments as possible ecological inorganic pigments.
Lanthanum based pigments: Formulations were developed with varying lanthanum and first row transition metal ions viz., chromium, manganese and iron. Lanthanum chloride salt was employed in the study. The ratio of La to Cr/Mn/Fe was 1:0:1. Increase the temperature of 800 °C at a rate of 5 °C/min. The maximum reflectance for the green pigment was around 550 nm and that for iron pigment was around 700 nm (Fig. 2). Accordingly the CIELAB colour coordinates varied and are presented (Table-1). The Cr and Mn based pigments were of greenish-yellow and that of Fe was more in the orange side [9,10]. In the absence of lanthanum, the purer oxides of chromium, manganese and iron were formed. There was significant change in the a* and b* values in the pigments formed with Cr and Fe, while no such change was observed with Mn.

Role of associated ion in the colour of pigment: When the chloride ion in lanthanum was replaced with acetate or carbonate, no significant change in the colour. In the pigments, when chloride ion was replaced with acetate and carbonate for a La:Fe Pigment [11], the bandgap energy (eV) changed from 2.103 to 2.39 and 2.47 respectively (Fig. 3). An increase in the bandgap energy (eV) by 0.1 units as the anion was lost completely as CO₂ while a chloride ion would possibly be lost completely as CO₂ while a chloride ion would possibly be.

CIE illuminant D65 was used in all the colour measurements. The CIELab (1976) colour space was used for colour measurement; the colourimetric values were computed using advanced spectroscopy software (Perkin Elmer).

The band gap values were calculated using Kubelk Munk function which is given by K-M = (1-R)²/2R, where R is the reflectance value. 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 (eV) = 1236/ wavelength (nm).

The hue angle h (Fig. 1) is defined as starting at + a* axis and is expressed in degrees. An h value of 90° would indicate yellow colour. Larger C* values indicate a higher Chroma or saturation. Chroma can also be referred to as cleanliness of the colour.
Role of cerium salt in colour of the cerium pigment:
When cerium carbonate, cerium sulfate, cerium oxalate, cerium acetate and cerium chloride were doped with ferrous sulfate [12] such that the Ce:Fe ratio was 1:0.1 (Table-3), the band gap energy varied as 2.08, 2.08, 2.7, 2.1 and 2.06 respectively (Fig. 5). A major shift in the band gap energy (eV) was observed only with cerium oxalate.

Role of cerium:metal ion ratio in colour of the cerium pigment:
When the cerium(III) chloride was maintained constant and the ratio of dopant varied such the resultant ratio was 10:1 to 10:5. The colour of the product is also changed as expected. There was no major change in the reflectance spectra, indicating that the colour remained more or less same. However, the intensity of the colour as reflected by a lower reflectance or in turn higher absorbance was seen as the dopant (Cr) concentration increased (Fig. 6).
Role of multiple doping in colour of the cerium pigment: When a single dopant was used the colour of the resulting pigment either reflected the colour of the dopant of that of cerium oxide. Multiple doping resulted in higher bandgap energy and lower L values (Table-4), indicating that the pigments had a much darker shade. The characteristic reflectance maxima were observed around 600 nm (Fig. 7). In the case of Ce:Mo:Fe [13], this reflectance maxima was very much pronounced and this corresponded to a bright orange colour, which was different from that of the individual dopants either alone or in combination (in the absence of cerium).

Development of paint and analysis of mass tone and tint strength: The developed pigment with combination of Ce:Mo:Fe in the ratio 1:0.1:0.01 was prepared in bulk at 1000 °C with a treatment temperature of 800 °C and duration of treatment of 120 min. A paint developed for the pigment had good mass tone and covering power and a reasonable tint strength. The associated ions did not have any significant influence on the colour of the pigment i.e. a cerium(III) chloride behaved more or less similar to that of cerium(III) carbonate and cerium(III) acetate. Individual doping resulted in colours, which were closer to either that of cerium oxide or the dopant oxide.

Multiple doping experiments revealed interesting results: An optimal doping of Ce:Mn:Fe and Ce:Mo:Fe resulted in better shades. The associated ions did not have any significant influence on the colour of the pigment i.e. a cerium(III) chloride behaved more or less similar to that of cerium(III) carbonate and cerium(III) acetate. Individual doping resulted in colours, which were closer to either that of cerium oxide or the dopant oxide.

![Fig. 7. Reflectance spectra of Ce:M1:M2 at 1.0:0.1:0.1 ratio](image)

**Fig. 7.** Reflectance spectra of Ce:M1:M2 at 1.0:0.1:0.1 ratio

**Table 4: Colour Coordinates for Ce:M1-M2 Pigments at Varying Ratios**

<table>
<thead>
<tr>
<th>Cerium salt</th>
<th>L</th>
<th>a*</th>
<th>b*</th>
<th>h*</th>
<th>C</th>
<th>Bandgap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M₁-Cr, M₂-Mo</td>
<td>27.7</td>
<td>7.1</td>
<td>16.4</td>
<td>66.6</td>
<td>17.9</td>
<td>2.2</td>
</tr>
<tr>
<td>M₁-Cr, M₂-Mn</td>
<td>30.9</td>
<td>3.2</td>
<td>23.3</td>
<td>82.2</td>
<td>23.5</td>
<td>2.3</td>
</tr>
<tr>
<td>M₁-Cr, M₂-Fe</td>
<td>19.3</td>
<td>5.5</td>
<td>16.5</td>
<td>71.7</td>
<td>17.3</td>
<td>2.2</td>
</tr>
<tr>
<td>M₁-Mn, M₂-Mo</td>
<td>48.6</td>
<td>9.7</td>
<td>25.2</td>
<td>68.9</td>
<td>26.9</td>
<td>2.1</td>
</tr>
<tr>
<td>M₁-Mn, M₂-Fe</td>
<td>38.2</td>
<td>1.2</td>
<td>9.7</td>
<td>82.9</td>
<td>9.8</td>
<td>2.2</td>
</tr>
<tr>
<td>M₁-Fe, M₂-Mo</td>
<td>40.1</td>
<td>12.0</td>
<td>44.2</td>
<td>74.9</td>
<td>45.7</td>
<td>2.3</td>
</tr>
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</table>

![Fig. 8. Mass tone (left) and tint strength (right) of developed Ce-Mo-Fe pigment](image)

**Fig. 8.** Mass tone (left) and tint strength (right) of developed Ce-Mo-Fe pigment

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Reflectance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>35</td>
</tr>
<tr>
<td>500</td>
<td>50</td>
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<tr>
<td>600</td>
<td>65</td>
</tr>
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<td>700</td>
<td>80</td>
</tr>
<tr>
<td>800</td>
<td>95</td>
</tr>
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</table>

**Development of paint and analysis of mass tone and tint strength:** The developed pigment with combination of Ce:Mo:Fe in the ratio 1.0:0.1:0.01 was prepared in bulk at 100 g quantities [14,15]. The paint thus developed was coated on a checkered board having a white and black background. The ability of the pigment to cover the black reflected its mass tone or hiding power (Fig. 8). The ability of the pigment to retain its colour when mixed with 5 parts of titanium dioxide for every part of the pigment corresponded to the tint strength of the pigment.

**Conclusion**

A replacement for cadmium, cobalt, lead and mercury based pigments has been sought through the use of rare earth metal ions – cerium and lanthanum. Solid state reactions of these metal ions with transition metal ions like chromium, molybdenum, manganese and iron were carried out individually. The reflectance spectra, band gap energy (eV), CIELAB colour coordinates were measured and the colour of the developed pigments characterized. It was found that cerium offered better scope for doping than lanthanum as it produced...