Synthesis and Characterisation of Rare Earth Oxide Based Pigments

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An attempt has been made to prepare eco-friendly pigments, stable at high temperature, based on rare earth metal oxides as replacement to the presently available inorganic products based on lead, chromium, cadmium, and mercury which are harmful to environment. As a first step, brilliant red pigments, ranging from chocolate (ISC 451) to crimson red (ISC 540) were prepared by calcination of cerium oxalate mixed with praseodymium oxide in varying proportions where the later acts as the chromophore. Sodium chloride in the precursor works as a modifier to improve the colour quality. Proper mixing of the ingredients and calcination at 1100°C are required for the formation of pigments with the desired characteristics.

Introduction

The modern coating system requires pigments which besides being strong and attractive, should be eco-friendly. This has led to a search for replacement of pigment formulations based on lead, chromium and cadmium; these are of polluting nature and not safe for use in certain materials especially ceramics, toys, and food contacts. Moreover, use of cadmium based pigments in polymers such as, polyvinyl chloride, polyurethane and cellulose acetates has been banned through a directive from the European Union. For the preparation of eco-friendly pigments, recent focus of scientists is on the rare earth metals. These are a group of 17 metals which are rarely available on earth’s crust but abundantly stored deep down. Their unique electronic structure imparts them incredible physical, chemical and magnetic properties, resulting in their extensive use in ceramic, pigment, automotive, and television industries. Because of their eco-friendly nature, resistance to corrosion and stability even at high temperature, these are of great importance not only for toy making and automotive industries but also for ceramic industries. The most popular of these rare earth based products are the red pigments. Addition of praseodymium(IV) oxide to refractory grade cerium(IV) oxide and its stabilisation leads to a cerium-rich solid solution in the red colour range. Maestro and Tatsu have prepared such red pigments for ceramics having the chemical composition of $\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_2$ from solutions of cerium nitrate, praseodymium nitrate and diammonium oxalate and calcining the dried sample at 1400°C, while Tumanov and Pavlova have employed a solid state reaction of cerium and praseodymium oxides at 1300 to 1320°C.

The present study is an attempt to synthesise and characterise rare earth oxide based red pigments from cerium oxalate and praseodymium oxide at relatively lower temperatures in the presence of a mineraliser. The effects of Ce and Pr ratio, calcination temperature and mineraliser on the shade of the pigment have been studied.

Materials and Methods

Materials

Reagent grade sodium chloride supplied by E.Merck, technical grade cerium(III) oxalate supplied by Fluka and praseodymium oxide supplied by The Indian Rare Earths, Ltd. were utilised for our study. Dibutyl phthalate has been used as the carrier oil for oil absorption studies and colour matching.

Method of Preparation

Red pigments consisting of cerium and praseodymium oxides were prepared by calcination of an intimately mixed and dried precursor of cerium (III) oxalate and praseodymium oxide ($\text{Pr}_6\text{O}_{11}$) obtained from Indian Rare
Earth's Ltd. along with 10 per cent sodium chloride as modifier. The ratio of cerium oxide to praseodymium oxide in the product was varied from 5 to 15:1. After calcination of the mixture at 1100°C, for 6h the resultant product was subjected to wet grinding, washing, drying, and powdering. Only the samples prepared with cerium oxide to praseodymium oxide ratios of 5:1, 10:1 and 15:1, along with sodium chloride at 1100°C were considered for characterisation studies due to their visibly acceptable colour shades.

**Oil Absorption and Bulk Density**

Methods for measuring the oil absorption capacities and bulk densities of the samples have been described earlier. Dibutyl phthalate has been used as the carrier oil for oil absorption capacity measurement. The results are presented in Table 1.

### Table 1— Oil absorption, bulk density, average particle size and surface area of the pigments

<table>
<thead>
<tr>
<th>CeO₂:PrO₁₅</th>
<th>Oil absorbed mL/kg</th>
<th>Bulk density kg/L</th>
<th>Average particle size μm</th>
<th>Surface area sq mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>5:1</td>
<td>231.7</td>
<td>1.32</td>
<td>3.90</td>
<td>1828.2</td>
</tr>
<tr>
<td>10:1</td>
<td>255.0</td>
<td>1.40</td>
<td>5.20</td>
<td>1323.2</td>
</tr>
<tr>
<td>15:1</td>
<td>300.0</td>
<td>1.47</td>
<td>7.49</td>
<td>908.4</td>
</tr>
</tbody>
</table>

**Colour Matching**

After measuring the oil absorption capacities, the same samples were painted on glazed ceramic tiles and their colours were matched with standard Indian colours. The results are presented in Table 2.

### Table 2— Colour matching of the pigments

<table>
<thead>
<tr>
<th>CeO₂:PrO₁₅</th>
<th>Colour</th>
<th>Matching Indian standard colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>5:1</td>
<td>Chocolate</td>
<td>ISC 451, Chocolate</td>
</tr>
<tr>
<td>10:1</td>
<td>Red</td>
<td>ISC 448, Deep Indian red</td>
</tr>
<tr>
<td>15:1</td>
<td>Red</td>
<td>ISC 540, Crimson red</td>
</tr>
</tbody>
</table>

**XRD, Particle Size and Surface Area**

X-ray diffractogram (Figure 1) of the representative sample with a cerium oxide to praseodymium oxide ra-
ratio of 15:1 was obtained, using a Philips Diffractometer Model PW-1400. The $d$-values were found out corresponding to the 2θ values and compared with those of cerium oxide and praseodymium oxide, given in the X-ray data file. Particle size distribution of the samples was measured by Malvern Particle Size Analyzer Model 3600, utilizing laser beam technique. This instrument, after measuring their spherical volumes, calculates the diameters of the particles and also their top surface area in sq m/mL. The average particle sizes and surface areas of the samples prepared at the three varying ratios are included in Table 1 and the total particle size distribution of these pigments is included in Table 3.

**Results and Discussion**

As is observed from the X-ray diffractogram of a representative sample with a cerium oxide to praseodymium oxide ratio of 15:1 (Figure 1), the strongest line with a $d$ value of 3.12(100) matches well with the strongest line of CeO$_2$ with a $d$ value of 3.12(100) and that of PrO$_{1.83}$ with a $d$-value of 3.15(100). All other lines also match 7 simultaneously with those of CeO$_2$ and PrO$_{1.83}$. Based on the initial composition of the mixture and the X-ray diffraction data, it may be concluded that the product is a solid solution of the oxides having, composition of Ce$_{1-x}$Pr$_x$O$_{1.28}$, where $x$ has values of 0.2, 0.1 and 0.067 when cerium oxide to praseodymium oxide ratio is 5, 10 and 15, respectively.

The particle size of a pigment influences its scattering efficiency which, in turn, determines its optical performance. The optical performance falls rapidly with increase in particle size. The finer the particle size the higher is its surface area and the better is its optical performance and tendency for dispersion in the matrix. Therefore, pigments having higher surface area and finer particle size are preferred for industrial applications. It is observed from Table 1 that the average particle size of the prepared samples varies from 3.9 to 7.49μm, which compares well with those of standard pigments (0.5 to 10μm). From Table 3, it is evident that nearly 89 per cent of the sample has particles of 7.88μm size at a CeO$_2$/PrO$_{1.83}$ ratio of 5:1. As the PrO$_{1.83}$ content decreases, this percentage comes down to 79 when CeO$_2$/PrO$_{1.83}$=10 and to 53 when CeO$_2$/PrO$_{1.83}$=15. Similar trend is observed with finer particles also. The percentage of 2.41μm particles, decreases from 13 through 5.5 to 1.2, as the respective CeO$_2$/PrO$_{1.83}$ ratio changes from 5:1 through 10:1 to 15:1. It can be inferred from the above, that an increase in PrO$_{1.83}$ content results in the enhancement of finer particles. This decrease in particle size with increase in PrO$_{1.83}$ content, suggests the possibility of achieving optimal balance between particle size and shade through variation of the ratio of the constituents. As seen from Table 3 the percentage of very fine particles, i.e., those having size in the range of less than 2μm is 6.9 for the sample with CeO$_2$/PrO$_{1.83}$(5:1), 2.8 for the sample with CeO$_2$/PrO$_{1.83}$(10:1) and 0.5 for the sample with CeO$_2$/PrO$_{1.83}$(15:1), which is not high enough to cause dust
handling and inhalation problems during subsequent handling of this pigment.

Since the pigments used for paints and inks are purchased by weight and sold by volume after dispersing them in a carrier oil, bulk density and oil absorption play important roles in deciding the cost. The lower these values the less is the cost of the paint. It is observed from Table 1 that the oil absorption capacity of the pigments lies in the 231-300mL/kg range which is much less than that of the established iron oxide red pigment (500mL/kg); these values vary inversely with the proportion of PrO$_{1.85}$ in the product. The bulk densities of these pigments are also low (1.32-1.47kg/L), thereby suggesting that the paints prepared from these pigments can be made available at a reasonable cost.

The primary function of a pigment is to impart the required colour by absorption of light of a certain wave length. The colour observed is the complement of the wave length absorbed. Though it is difficult to quantify, human eye is considered to be one of the most sensitive instruments to evaluate a colour, through comparison, with a standard colour. In the pigments studied, praseodymium oxide acts as the chromophore. According to Joergensen and Rittershausen the red colour of the praseodymium oxide powder is related to a charge transfer band due to charge transfer from the ligand orbital to the Pr$^{3+}$ cation. As evident from Table 2, colours of these pigments vary from chocolate (at CeO$_2$/PrO$_{1.85}$ ratio of 5:1), matching with the Indian Standard Colour (ISC) 451 to crimson red (at CeO$_2$/PrO$_{1.85}$ ratio of 15:1) matching with ISC 540. Immediately at the CeO$_2$/PrO$_{1.85}$ ratio of 10:1, a deep Indian red colour matching with ISC 448 is produced. This indicates the role of PrO$_{1.85}$ in deepening the colour. However, the presence of a mineraliser imparts the required brightness to the colour by modifying and catalysing the reaction, followed by stabilisation of the crystal structure of the pigment. In the present study the ingredients were mixed thoroughly with sodium chloride before subjecting to calcination. The bright colour in the presence of NaCl and the dull colour in its absence, suggest its role as a modifier and catalyst. As a dull coloured product was obtained at <1100°C, it may be inferred that incorporation of the coloured ion into the crystal lattice of CeO$_2$ takes place through a solid state chemical reaction at elevated temperatures and NaCl stabilises the crystal structure of the pigment.

Conclusions

(i) Eco-friendly red pigments matching with the established products can be prepared by calcination of cerium oxalate and praseodymium oxide.
(ii) The samples exhibit colours varying from chocolate (ISC 451) to crimson red (ISC 540) with varying initial concentrations of the ingredients.
(iii) Sodium chloride acts as an accelerator to the solid state reaction, while also acting as a modifier to impart the required brightness to the colour and stabilizes the crystal structure of the pigment at higher temperatures.
(iv) Praseodymium oxide content in the precursor plays an important role in deciding the particle size and shade of the pigment.
(v) Calcination at 1100°C is sufficient for the formation of the desired pigment.

Acknowledgments

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References