Compounds Based on dDped Bi$_2$O$_3$ as New Ecologically Friendly Yellow–Orange Shade Pigments

Petra Šulcová
University of Pardubice, Czech Republic

Nataliia Gorodylova
University of Pardubice, Czech Republic

INTRODUCTION

High performance inorganic pigments are an integral part of a range of decorative and protective coatings and are widely used in various areas of application including paints, inks, plastics, rubbers, glass, cement, porcelain enamels and glazes (Smith, 2002). Unfortunately, the majority of yellow inorganic pigments which are currently employed in these applications contain toxic metals such as cadmium, lead or chromium (VI). Nowadays these colorants, including red lead, lead molybdate and chrome orange are considered as ecologically harmful and their application is limited due to new laws and regulations in the ecological and toxicological field. As a result, continuous research has been started at our department with the goal to displace the well-known and widely used harmful pigments by environmentally friendly or less toxic substances with high performing characteristics. The summary of our study which is presented in this article is dedicated to new environmentally benign inorganic pigments based on bismuth oxide, which supersede the harmful yellow-orange pigments by their coloring performance and thermal stability.

BACKGROUND

Natural inorganic pigments, derived mainly from mineral source, have been known since prehistoric times and human history is rich with examples of their use. The first clear yellow pigments, orpiment (arsenic sulfide) has been found on wall paintings in Giza dated as early as 4000 BC. In ancient Egypt and later in Assyria and China, this yellow colorant was prepared by grinding of the naturally occurring mineral of the same name, i.e. Orpiment. Recent archeological findings documented its use by our ancestors for aesthetic, religious and other purposes. By the way, the preservation of primitive pictures drawn thousands years ago, demonstrate one of the strongest aspects of inorganic pigments – their long lasting stability.

One of the first synthetic yellow pigments we know of is called Naples yellow (lead antimonite). Moreover, it is one of the oldest synthetic pigments, dating from around 1620. Naples yellow was used extensively by the old masters and well into the 20th century. The genuine pigment is toxic, and its use today is becoming increasingly rare. Typical modern yellow pigments include chromate compounds of lead, cadmium sulphides and bismuth vanadates (Buxbaum, 2005). The important characteristics of these pigments, including composition, refractive index, density and covered color range are summarized in Table 1.

Chromate pigments mainly consist of lead chromates (chrome yellow and chrome orange) and mixed lead chromate-molybdates (molybdate orange and molybdate red) whose color range varies from light lemon to red. Chrome yellow pigments consists of Pb(Cr,S)O$_4$ and chrome orange is a basic lead chromate, PbCrO$_4$·PbO. Molybdate red and molybdate orange are mixed-phase pigments with formula Pb(Cr,Mo,S)O$_4$. Most commercial products of molybdate red show a MoO$_3$ content of 4 – 6 %. Their color hue mainly depends on a molybdate content, crystal morphology and particle size, which can be varied in order to obtain the
required coloristic properties. Just like chrome yellows and oranges, molybdate orange and red are obtained by precipitation of lead salts with alkali chromates, ammonium molybdate and sulfuric acid. By controlling the pH value and synthesis temperature, the particle size and, thus, the color hue of these compounds can be easily varied (Buxbaum, 2005). Chrome pigments are widely used in paints, coatings and plastics (e.g. polyethylene, polyesters, polystyrene), and are characterized by brilliant color hues, good tinting strength, hiding power, lightfastness and weather resistance.

Another important group of yellow-shade pigments is represented by compounds containing cadmium. In the pigment industry the term “cadmium pigments” is commonly used to refer to pure sulfides and sulfosalts of cadmium. Cadmium sulfide occurs naturally as a cadmium blende or greenockite, however the mineral itself does not have any pigment properties. The color of cadmium pigments can be controlled via the composition and the size of the primary particles. It covers a wide range from light to deep yellow, where selenium additions allow the hues to change from orange and red to bordeaux (Table 1). To basic manufacturing processes for cadmium pigments can be distinguished: firstly the precipitation process of cadmium salts with a sodium polysulfide, and, secondly, the powder process, where finely divided cadmium carbonate or cadmium oxide is intensively mixed with sulfur and subjected to calcination. These pigments provide an excellent hiding power and have found application in the coloring of plastics and ceramics.

Bismuth vanadate pigments are a relatively new pigment class that steadily gained importance over the last two decades. The pigments with a composition range $\text{BiVO}_4 \cdot 3\text{Bi}_2\text{MoO}_6$ exhibit brilliant greenish yellow to reddish yellow shades (Table 1). Bismuth vanadate was described for the first time in a medical patent in 1924 and synthesized as a solid substance in 1964. In 1976, Du Pont described the preparation and properties of “brilliant primrose yellow” monoclinic $\text{BiVO}_4$. Montedison developed numerous pigment combinations based on $\text{BiVO}_4$, for example $\text{BiVO}_4 \cdot \text{Bi}_2\text{XO}_6$, where $\text{X}$ is Mo or W. Typically, they are obtained by a precipitation process in which caustic soda or sodium hydroxide is added to a solution containing bismuth nitrate, sodium vanadate, sodium molybdate and nitric acid. Thermstable modifications of these pigments are available today providing heat stability up to 260 - 280 °C (Buxbaum, 2005). Bismuth vanadates are high performance lead- and chromate-free inorganic yellow pigments, which are widely used in the coating industry to manufacture brilliant yellow, orange, red and green shades with good gloss and hiding power. These pigments have benefited from the decline in use of lead chromate and cadmium pigments, especially in the coating and plastic industries, however they lie in a higher price range segment of inorganic pigments due to costliness of the raw materials.

From the brief introduction to the modern yellow-shade pigments, it is evident that the majority of today’s industrially used colorants contain toxic metals such as cadmium, lead and hexavalent chromium. In spite of the strict limitation in their application existing alternative compounds are not able to compete with these pigments due to their excellent performance and for this reason can’t supersede them in many industrial fields. Thus, a serious need arises to discover new high performance, environmentally friendly and economically viable materials, which would be able to replace the toxic inorganic pigments.

From this point of view, compounds on basis of $\text{Bi}_2\text{O}_3$, which belong to inorganic pigments of the oxide type, seem to be interesting due to their color varying

**Table 1. General characteristics of the most important yellow-shade pigments (Buxbaum, 2005)**

<table>
<thead>
<tr>
<th>Pigment</th>
<th>Composition</th>
<th>Refractive Index</th>
<th>Density, g·cm⁻³</th>
<th>Color Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chrome yellow</td>
<td>Pb(Cr,S)O₄</td>
<td>2.3 - 2.65</td>
<td>6</td>
<td>light lemon - reds</td>
</tr>
<tr>
<td>Chrome orange</td>
<td>PbCrO₄·PbO</td>
<td>2.4 - 2.7</td>
<td>6 - 7</td>
<td></td>
</tr>
<tr>
<td>Molybdate red/ molybdate orange</td>
<td>Pb(Cr,Mo,S)O₄, MoO₃, 4 – 6 %</td>
<td>2.3 - 2.65</td>
<td>5.4 - 6.3</td>
<td></td>
</tr>
<tr>
<td>Cadmium pigments</td>
<td>(Cd,Zn)(S,Se)</td>
<td>2.5 – 2.8</td>
<td>4.2 - 5.6</td>
<td>light yellow - orange - bordeaux</td>
</tr>
<tr>
<td>Bismuth vanadates</td>
<td>BiVO₄·3Bi₂MoO₆</td>
<td>2.45</td>
<td>5 - 7</td>
<td>brilliant greenish yellow - reddish yellow</td>
</tr>
</tbody>
</table>