

# THE EFFECT OF MINERALIZERS ON PIGMENTARY PROPERTIES OF CASSITERITE PIGMENTS DOPED BY MANGANESE IONS

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## Abstract

The compounds of formula  $\text{Sn}_{0.752}\text{Co}_{0.08}\text{P}_{0.16}\text{Mn}_{0.008}\text{O}_2$  were prepared by classical ceramic method. The selected mineralizers ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$ ,  $\text{MgCl}_2\text{-MgO}$  (1:1),  $\text{LiF}$ ,  $\text{Li}_2\text{CO}_3$ ,  $\text{CaCl}_2$ ) were used in amount of 5 wt. % at the preparation of pigments. The reaction mixtures were calcinated in the electric furnace at synthesis temperatures 1200 – 1500 °C for 3 hours. After calcination, prepared pigments were milled in vibration mill for 30 seconds. The goal was to assess the effect of mineralizers on pigmentary properties of final compounds. The synthesised pigments were characterised in terms of colour properties after their application into the organic binder. They were also studied with respect to their phase composition as well as the particles size distribution.

## Introduction

The inorganic pigments are a fundamental part of many decorative and protective coatings. As know, ceramic pigments are composed of metal oxide or metal oxide compounds<sup>1</sup>. Stannic pigments with the structure of cassiterite mineral are classified as the important ceramic pigments based on tin compounds. The cassiterite pigments are highly chemically and thermally stable ceramic pigments derived from tetragonal mineral cassiterite ( $\text{SnO}_2$ ) and they are used mainly to clouding of the glazes and enamels<sup>2</sup>. Tin dioxide (cassiterite) exhibits a rutile structure consisting of infinite chains of octahedral  $\text{SnO}_6$  linked by sharing of edges and corners to form a three-dimensional framework. This host lattice is suitable for the incorporation of colouring metal ions such as transition metals or the rare earth metals<sup>3</sup>. Tin dioxide is used as a host lattice for important ceramic pigments, e.g. Chrome Tin Orchid Cassiterite (CPMA No. 11–23–5), Tin Vanadium Yellow Cassiterite (CPMA No. 11–22–4) and Tin Antimony Grey Cassiterite (CPMA No. 11–24–8)<sup>4</sup>. By partial substitution of Sn (IV) ions (0.069 nm) for ions of suited chromophores, a colour change in originally colourless system is achieved. In this research the ions of cobalt and manganese as chromophores were chosen<sup>5</sup>. Due to Co ions (II) have oxidation state lower than (IV), a second element with oxidation state higher than (IV) is always added in order to fulfill the electroneutrality of the structure. In this case P (V) ions are used as charge-compensating elements.

The synthesis of cassiterite pigments occurs most efficiently at high calcination temperatures (1350 – 1600 °C) and therefore their production can be energetically and economically demanding<sup>6</sup>. In order to reduce calcination temperature and to support the solid state reaction, they were added substances with mineralization effect into the reaction mixtures. The mineralizers provide a liquid medium and increase the diffusion rate between the reactives, thereby speeding up the reaction. The most commonly used mineralizers are carbonates, hydroxides and halides<sup>7</sup>.

## Experimental

The powder synthesis was carried out by ceramic method, based on the solid state reaction. The starting materials used for preparation of  $\text{Sn}_{0.752}\text{Co}_{0.08}\text{P}_{0.16}\text{Mn}_{0.008}\text{O}_2$  pigments were  $\text{SnO}_2$  (>99.9%, Alfa Aesar, Germany),  $\text{Co}(\text{OH})_2$  (99%, Shepherd Color Company, USA),  $\text{NH}_4\text{H}_2\text{PO}_4$  (99.5%, Lachema a.s., Czech Republic) and  $\text{MnO}_2$  (>99.9%, Lachema a.s., Czech Republic) weighed in suitable molar proportion and subsequently ground manually in a porcelain mortar to obtain a homogenous reaction mixture. The mineralizers ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$ ,  $\text{MgCl}_2\text{-MgO}$  (1:1),  $\text{LiF}$ ,  $\text{Li}_2\text{CO}_3$ ,  $\text{CaCl}_2$ ) were used in amount of 5 wt. % at the preparation of pigments. The mixtures with mineralizers were calcinated in corundum crucibles in an electric resistance furnace. The heating of furnace was programmed with increasing temperature at a rate  $10 \text{ °C} \cdot \text{min}^{-1}$  and the calcination temperature of 1200 – 1450 °C was maintained for three hours. All samples were gradually cooled to room temperature and ground in an agate mortar.

The prepared pigments were applied to organic matrix (dispersive acrylic paint Parketol, Balakom, a.s., Czech Republic) in mass tone. For testing in the organic binder, the suspension containing 1 g of the sample and 1.5

cm<sup>3</sup> of binder was homogenized. This suspension was converted by a pestle to dense paste able to flowing. The coloured coating films were prepared by application of the paste on white nonabsorbing glossy paper. The coating layer of film was created by dragging the Bird's applicator. The prepared coating films were kept to dry spontaneously in the open air. Then they were ready for an evaluation of colour properties of pigments into organic binder in mass tone.

The optical properties of pigments and their applications were measured by spectrophotometer ColourQuest XE (HunterLab, USA). The measurement conditions were the following: an illuminant D65, 10° complementary observer and measuring geometry d/8°. The values  $a^*$  (the red-green axis) and  $b^*$  (the yellow-blue axis) indicate the colour hue. The value  $L^*$  represents the lightness or darkness of the colour as related to the natural grey scale. In the  $L^*a^*b^*$  system, it is described by numbers from 0 (black) to 100 (white). The value  $C$  (Chroma) represents saturation of the colour and determines colour purity. The colour hue of pigments is also possible to express as a hue angle  $H^\circ$ . Hue angle  $H^\circ$  is defined as starting at the  $+a^*$  axis and indicates the position of the sample in  $a^*$ ,  $b^*$  diagram. It is expressed in degrees;  $H^\circ = 350-35^\circ$  (for red),  $H^\circ = 35-70^\circ$  (for orange),  $H^\circ = 70-105^\circ$  (for yellow),  $H^\circ = 105-195^\circ$  (for green),  $H^\circ = 195-285^\circ$  (for blue),  $H^\circ = 285-350^\circ$  (for violet). Chroma  $C$  and hue angle  $H^\circ$  of samples were calculated according to the Eqs. (1) and (2)<sup>7</sup>.

$$C = (a^{*2} + b^{*2})^{1/2} \quad (1)$$

$$H^\circ = \arctg(b^*/a^*) \quad (2)$$

The crystal structures of the powdered materials were studied by X-ray diffraction analysis. The phase composition was determined using diffractometer Empyrean (PANalytical, Netherlands). The particle size distribution of the synthesised pigments was measured using an equipment Mastersizer 2000/MU (Malvern Instruments, Ltd., UK). This device provides volumetric distribution and uses the laser diffraction on particles dispersed in a liquid medium. The pigments were ultrasonically homogenized in solution of  $\text{Na}_4\text{P}_2\text{O}_7$  ( $c = 0.15 \text{ mol dm}^{-3}$ ) for 120 s. The signal was evaluated on the basis of Fraunhofer diffraction. The measurement is performed in three steps, the results are automatically calculated as average and presented as  $d_{10}$ ,  $d_{50}$ ,  $d_{90}$  and *span* values.

$$\textit{span} = (d_{90} - d_{10})/d_{50} \quad (3)$$

## Discussion and result analysis

### X-ray diffraction analysis

The synthesised powder compounds were studied by XRD analysis. The diffractograms of the samples were two-phased, eventually three-phased at all synthesis temperatures. The only exceptions were pigments with mineralizer  $\text{CaCl}_2$ , which were single-phased at calcination temperature up to 1300 °C. The major crystalline phase corresponded with the tetragonal structure of  $\text{SnO}_2$  (JPDF No. 00-041-1445) with  $P4_2/mnm$  symmetry was observed. Other crystalline phases were detected in very low intensities and their intensities were not changing with increasing calcination temperature. The presence of secondary, eventually tertiary phases affected the colour properties and the particle size distribution as well.

Table I

The summary of results from XRD analysis of  $\text{Sn}_{0.752}\text{Co}_{0.08}\text{P}_{0.16}\text{Mn}_{0.008}\text{O}_2$  pigments synthesised at temperature 1250 °C with mineralizers

| Mineralizer   | Detected phases                          | Crystal structure | PDF card    |
|---|--|-------------------|-------------|
| $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$ | $\text{SnO}_2$                           | tetragonal        | 00-041-1445 |
|   | $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ | monoclinic        | 00-044-0071 |
| $\text{MgO-MgCl}_2$   | $\text{SnO}_2$                           | tetragonal        | 00-041-1445 |
|   | $\text{Co}_2\text{SnO}_4$                | cubic             | 04-006-5703 |
|   | $\text{Mg}_3(\text{P}_2\text{O}_8)$      | monoclinic        | 01-079-8260 |
| $\text{CaCl}_2$   | $\text{SnO}_2$                           | tetragonal        | 00-041-1445 |
|   | $\text{CaSn}_4(\text{PO}_4)_6$           | rhombohedral      | 04-016-8448 |
| $\text{LiF}$  | $\text{SnO}_2$                           | tetragonal        | 00-041-1445 |
|   | $\text{LiCoPO}_4$                        | orthorhombic      | 01-078-5576 |
| $\text{Li}_2\text{CO}_3$                                      | $\text{SnO}_2$                           | tetragonal        | 00-041-1445 |
|   | $\text{LiCoPO}_4$                        | orthorhombic      | 01-078-5576 |

#### The colour properties

The colour coordinates of pigments synthesised using mineralizers  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$ ,  $\text{MgO-MgCl}_2$  and  $\text{CaCl}_2$  are shown in the table (Tab. II). They have obtained the violet shades at pigments when borax was used as a mineralizer. This type of mineralizer provided the highest saturation at calcination temperature 1300 °C. The increase of saturation was caused by the significantly higher contribution of the red shade. The violet colouration was probably strengthened by the presence of secondary crystalline phase –  $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ . The coordinate  $L^*$  (lightness) had irregular trend and this value was decreasing from temperature 1300 °C. In the case, when the mixture of  $\text{MgO}$  and  $\text{MgCl}_2$  (in ratio 1:1) was used as a mineralizer, grey and grey-blue shades were obtained. This grey coloration is caused by very low value  $C$  (saturation), especially at higher calcination temperatures. These pigments presented the lowest values of lightness as well. We can conclude that the using  $\text{MgO-MgCl}_2$  as a mineralizer has proved to be the least suitable. They were obtained uninteresting colour shades with low saturation. If we are talking about pigments with mineralizer  $\text{CaCl}_2$ , we can say that they were obtained pigments, whose colour was shifted closer toward to red-violet then predicted blue-violet colouration. The pigments had reddish colouration up to temperature 1300 °C. It was caused by the presence of secondary crystalline phase -  $\text{CaSn}_4(\text{PO}_4)_6$ . These pigments had higher values of  $L^*$  and they seemed lighter. Above the temperature 1300 °C, the pigments were single-phased and this fact affected the colouration of the pigments. The remaining pigments had the blue-violet colouration. The contribution of the blue shade ( $-b^*$ ) was increasing up to 1400 °C.

The colour coordinates of pigments synthesised using mineralizers  $\text{LiF}$  and  $\text{Li}_2\text{CO}_3$  are shown in the table (Tab. III). These types of mineralizers provided the lightest colour shades. It was obvious from the values of colour coordinate  $L^*$ . These values of  $L^*$  were in the range from approx. 55 to 76. In the case of using  $\text{LiF}$  as a mineralizer, the blue-violet colour shades were obtained. The best results provided pigments, synthesised in temperature range from 1300 to 1400 °C. These pigments seems darker with higher contribution of red and blue colour shade. Last but not least  $\text{Li}_2\text{CO}_3$  was used as a mineralizer. From presented results was clear, that these pigments were the lightest. The pigments with the highest saturation  $C$  were obtained in temperature range from 1200 to 1250 °C. These pigments provided blue-violet colouration with higher contribution of blue shade ( $-b^*$ ). The fact is, that pigments synthesised at 1450 °C had almost the same colouration as pigments with using  $\text{CaCl}_2$  as a mineralizer at calcination temperature 1400 °C.

Table II

The colour coordinates and the particle size distribution of  $\text{Sn}_{0.752}\text{Co}_{0.08}\text{P}_{0.16}\text{Mn}_{0.008}\text{O}_2$  pigments synthesised using mineralizers  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$ ,  $\text{MgO-MgCl}_2$  (1:1) and  $\text{CaCl}_2$

| Mineralizer   | Temperature [°C] | L*    | a*    | b*     | C     | H°     | $d_{50}$ [µm] | span |
|---|------------------|-------|-------|--------|-------|--------|---------------|------|
| $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$ | 1200             | 51.59 | 9.34  | -21.74 | 23.66 | 293.25 | 4.2           | 4.0  |
|   | 1250             | 51.61 | 8.46  | -19.95 | 21.67 | 292.98 | 3.9           | 4.1  |
|   | 1300             | 52.82 | 10.82 | -23.64 | 26.00 | 294.59 | 2.1           | 3.3  |
|   | 1350             | 50.95 | 8.28  | -19.39 | 21.08 | 293.12 | 2.8           | 3.3  |
|   | 1400             | 50.14 | 5.11  | -15.86 | 16.66 | 287.86 | 2.2           | 2.6  |
|   | 1450             | 48.79 | 3.29  | -13.43 | 13.83 | 283.76 | 3.6           | 6.1  |
| $\text{MgO-MgCl}_2$ (1:1)                                     | 1200             | 51.35 | -4.21 | -9.86  | 10.72 | 246.88 | 2.1           | 7.2  |
|   | 1250             | 48.65 | -3.80 | -8.45  | 9.27  | 245.79 | 2.1           | 5.1  |
|   | 1300             | 50.15 | -3.69 | -8.31  | 9.09  | 246.06 | 2.4           | 2.6  |
|   | 1350             | 45.57 | -2.90 | -5.03  | 5.81  | 240.03 | 2.9           | 6.6  |
|   | 1400             | 45.57 | -2.50 | -5.11  | 5.69  | 243.93 | 2.1           | 2.8  |
|   | 1450             | 48.77 | -3.36 | -3.50  | 4.85  | 226.17 | 2.4           | 4.5  |
| $\text{CaCl}_2$   | 1200             | 64.12 | 13.19 | -5.01  | 14.11 | 339.20 | 1.9           | 9.5  |
|   | 1250             | 57.80 | 12.71 | -9.81  | 16.06 | 322.34 | 1.8           | 4.1  |
|   | 1300             | 57.90 | 13.44 | -10.42 | 17.01 | 322.21 | 2.6           | 2.9  |
|   | 1350             | 54.29 | 11.16 | -15.85 | 19.38 | 305.15 | 1.8           | 3.4  |
|   | 1400             | 56.63 | 12.24 | -17.27 | 21.17 | 305.33 | 2.0           | 3.6  |
|   | 1450             | 54.52 | 8.34  | -11.99 | 14.61 | 304.82 | 2.0           | 4.1  |

Table III

The colour coordinates and the particle size distribution of  $\text{Sn}_{0.752}\text{Co}_{0.08}\text{P}_{0.16}\text{Mn}_{0.008}\text{O}_2$  pigments synthesised using mineralizers  $\text{LiF}$  and  $\text{Li}_2\text{CO}_3$

| Mineralizer              | Temperature [°C] | L*    | a*    | b*     | C     | H°     | $d_{50}$ [µm] | span |
|--------------------------|------------------|-------|-------|--------|-------|--------|---------------|------|
| $\text{LiF}$             | 1200             | 63.51 | 12.97 | -16.11 | 20.68 | 308.84 | 1.7           | 2.5  |
|                          | 1250             | 70.63 | 10.33 | -11.72 | 15.62 | 311.39 | 1.8           | 2.7  |
|                          | 1300             | 59.87 | 12.34 | -19.75 | 23.29 | 302.00 | 1.8           | 2.9  |
|                          | 1350             | 56.78 | 10.38 | -23.42 | 25.62 | 293.90 | 1.8           | 2.5  |
|                          | 1400             | 55.14 | 10.91 | -22.08 | 24.63 | 296.29 | 1.8           | 3.6  |
|                          | 1450             | 62.79 | 8.01  | -13.23 | 15.47 | 301.19 | 2.1           | 6.7  |
| $\text{Li}_2\text{CO}_3$ | 1200             | 59.13 | 9.87  | -21.58 | 23.73 | 294.58 | 1.6           | 2.2  |
|                          | 1250             | 59.69 | 12.60 | -19.39 | 23.12 | 303.02 | 1.6           | 2.5  |
|                          | 1300             | 75.54 | 7.15  | -8.97  | 11.47 | 308.56 | 1.7           | 3.3  |
|                          | 1350             | 59.98 | 12.85 | -12.97 | 18.26 | 314.73 | 1.9           | 4.0  |
|                          | 1400             | 57.94 | 12.33 | -13.27 | 18.11 | 312.90 | 1.8           | 4.0  |
|                          | 1450             | 56.96 | 13.75 | -17.07 | 21.92 | 308.85 | 2.1           | 3.1  |

#### The particle size distribution

The calcination temperature and type of mineralizer affect not only related colour properties but also particle size distribution. The particle size distribution belongs to the one of the most significant measured properties of synthesised powders and it can affect optical properties (final colour of pigments) and opacity. The values of the mean of the particle size  $d_{50}$  were in the range from approx. 1.6 to 4.2 µm. The presented results showed that the growing synthesis temperature caused an increase of values  $d_{50}$  in the case, where the  $\text{LiF}$  and  $\text{Li}_2\text{CO}_3$  were used as mineralizes. At these pigments, the parameter *span* showed, that wide of the particle size distribution was increasing with growing calcination temperature. In the remaining pigments the value of  $d_{50}$  had irregular trend with the increasing temperature. The recommended values of  $d_{50}$  are about 2 µm for using into the organic matrix. In some cases it will be necessary to reduce of values  $d_{50}$  by grinding or milling.

## Conclusion

The main aim of the research was to prepare blue-violet  $\text{Sn}_{0.752}\text{Co}_{0.08}\text{P}_{0.16}\text{Tb}_{0.008}\text{O}_2$  ceramic pigments. The samples were synthesised by the classical ceramic method which is based on solid state reaction. The calcination temperatures were chosen in the range of 1200–1450 °C. Studies of X-ray diffraction showed that two-phased, eventually three-phased samples were prepared at all calcination temperatures. The only exceptions were pigments with mineralizer  $\text{CaCl}_2$ , which were single-phased at calcination temperature up to 1300 °C. The presence of secondary, eventually tertiary phases affected the colour properties and the particle size distribution as well. The preferable mineralizers for preparation of cassiterite pigment are  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$  and  $\text{Li}_2\text{CO}_3$ . The  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$  as a mineralizer provided blue-violet or violet colour shades and  $\text{Li}_2\text{CO}_3$  as a mineralizer provided lavender-violet colour shades. These mineralizers showed positive effects at lowest synthesis temperatures. It can be evaluated positively especially from economic point of view. In the contrast, the least suitable mineralizer was proved  $\text{MgO-MgCl}_2$  (1:1). They were obtained grey-blue colour shades with low saturation. In the case of using  $\text{CaCl}_2$  as a mineralizer, they were obtained red-violet colour shades up to 1300 °C, above this temperature the pigments provided violet colour. The mineralizer  $\text{LiF}$  provided interesting violet colour shades in the temperature range from 1300 to 1400 °C, nevertheless at these calcination temperatures, their preparation is energetically and economically demanding. The values of the mean of the particle size  $d_{50}$  were in the range from approx. 1.6 to 4.2  $\mu\text{m}$ . The lowest values of  $d_{50}$  provided  $\text{LiF}$  and  $\text{Li}_2\text{CO}_3$  used as mineralizers. In the most of cases, the values of  $d_{50}$  were about 2  $\mu\text{m}$  and they are suitable for using into the organic matrix.

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