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Synthesis of $CoNH_4PO_4$ pigment by co-precipitation method

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For the preparation of the cobalt light-violet pigment ($CoNH_4PO_4 \cdot H_2O$), a simple co-precipitation method has been suggested. The characteristics of the obtained product were compared with those of a commercial sample purchased from Kremer Pigmente (Germany). The pigment specimens were characterized by X-ray diffraction analysis (XRD), infrared spectroscopy (IR) and scanning electron microscopy (SEM). The optical properties of both $CoNH_4PO_4 \cdot H_2O$ samples were also recorded. The formation of monophasic cobalt light-violet pigment by a simple co-precipitation method was confirmed by XRD analysis data. The SEM micrographs suggest that $CoNH_4PO_4 \cdot H_2O$ solids synthesized by co-precipitation are composed of irregular submicron grains with an average grain size of less than 5 μm.

Key words: pigments, cobalt light-violet, $CoNH_4PO_4 \cdot H_2O$, synthesis, co-precipitation method

INTRODUCTION

Ceramic pigments are important in the industry due to their applications in tableware, sanitaryware, tiles and glasses. They can be classified into two broad categories: a) idiochromatic (self-coloured) and b) allochromatic (other-coloured) pigments [1]. Cobalt-based ceramic pigments are widely used for coloured glazes in the ceramic industry for floor or wall whitewares, and also in the bulk coloration of polished, unglazed, porcelainized stoneware. They are characterized by a high resistance with respect to light, environment, high temperature and chemicals. These pigments are also used in many industries because of their different colour, fine particle size, good hiding power, acid acceptance and compatibility with many organic and inorganic systems [2, 3].

Recently, new cobalt-based ceramic pigments have been synthesized using different synthetic approaches. It is well known that cobalt silicates are well dispersed in glazes and coatings. A polycrystalline material with the qualities of a blue pigment has been obtained at low temperatures in the $CoO–ZnO–SiO_2$ system by the sol–gel technology [4]. The applicability of this method for the synthesis of pigments was also demonstrated. The classical Co olivine blue pigment (Co_2SiO_4) and Co-doped willemite ($Co_{0.05}Zn_{1.95}SiO_4$) were prepared by the traditional solid state reaction method [5]. The performance of Co^{2+}-olivine and Co^{2+}-willemite solid solutions as blue pigments has been compared [6]. The results have shown that the amount of Co introduced in the willemite lattice can be minimized to a great extent whilst maintaining an intense and pure blue colour.

Idiochromatic blue cobalt aluminate ($CoAl_2O_4$) and purple pyroborate ($Co_2B_2O_5$) were prepared by the solution combustion method [7]. It has been concluded that both pigments are voluminous, homogeneously coloured with a large surface area. Recently, a blue pearlescent pigment was obtained by coating microemulsion-synthesized $CoAl_2O_4$ nanoparticles onto mica titania [8]. Cobalt-doped alumina powders were synthesized by the polymeric precursor method to obtain a ceramic pigment [9]. γ-Al_2O_3 was crystallized at temperatures higher than 700 °C, remaining as a single phase to about 1000 °C in spite of the added cobalt percentage. From this, α-Al_2O_3 begun its formation together with $CoAl_2O_4$ spinel. The results also showed that the higher blue colour intensity was obtained for the powders

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with Co-doped γ-Al_2O_3 closest of phase transition to α-Al_2O_3 + $CoAl_2O_4$.

There are several ceramic pigments with a phosphate structure. For example, $Co_3(PO_4)_2$ and $FePO_4$ solid solutions ($Co_{3-x}Fe_xP_2O_{8+x/2}$) were synthesized by the chemical coprecipitation method [10]. The possibility of using cobalt molybdophosphates as pigments was also demonstrated [11].

There is a wide range of various historical cobalt pigments. The palette of their colours is pretty large: blue, green, yellow, violet, brown and black [12]. Some of them were more important in the history of painting, others were more often used for decorating ceramic works or producing ceramic glaze. The most important violet cobalt pigments are different phosphates: cobalt violet dark $Co_3(PO_4)_2$ and cobalt violet light $CoNH_4PO_4 \cdot H_2O$. The purpose of the present work was to prepare and characterize the cobalt light-violet pigment ($CoNH_4PO_4 \cdot H_2O$) by a simple co-precipitation method.

EXPERIMENTAL

For the preparation of cobalt light-violet pigment, analytical grade $CoCO_3$, $(NH_4)_3PO_4$ and H_3PO_4 were used as starting materials. Firstly, 2.38 g (20 mmol) of $CoCO_3$ was dissolved in 40 ml of 0.5 M H_3PO_4 at 65 °C. Secondly, to the above solution 5 g (33.5 mmol) of $(NH_4)_3PO_4$ dissolved in a small amount of distilled water was added. The obtained dark violet turbid solution was stirred for 1 h at the same temperature. Finally, the mixture was rapidly cooled within the ice bath. The obtained light-violet powders were dried at room temperature. The yield of the reaction product was calculated to be nearly 98%. For the interpretation, the properties of the synthesized $CoNH_4PO_4 \cdot H_2O$ sample were compared with those of the commercially available cobalt light-violet pigment (Kremer Pigmente, Germany).

The synthesized samples were characterized by X-ray powder analysis (XRD) performed with a D8 Bruker AXS powder diffractometer using $CuK\alpha_1$ radiation. The surface morphology and microstructure were estimated by electron scanning microscopy (SEM) with an EVO 50 XVP scanning electron microscope. The infrared (IR) spectra were recorded on a Perkin–Elmer FT-IR Spectrum BX II spectrometer. Samples before IR analysis were mixed (1.5%) with dried KBr and pressed into pellets. The optical reflection measurements of the pigment samples were carried out using an SF-56 spectrophotometer at room temperature with a fused-quartz glass substrate inserted into the reference beam path of the spectrophotometer.

RESULTS AND DISCUSSION

X-ray diffraction patterns of the synthesized pigment samples and those purchased from Kremer Pigmente are presented in Fig. 1. One can see that both XRD patterns are almost identical and fit very well the standard XRD pattern of ammonium cobalt phosphate hydrate (PDF [21–793]). Therefore, we can conclude from XRD data that the single phase cobalt light-violet pigment was synthesized using a simple co-precipitation approach.

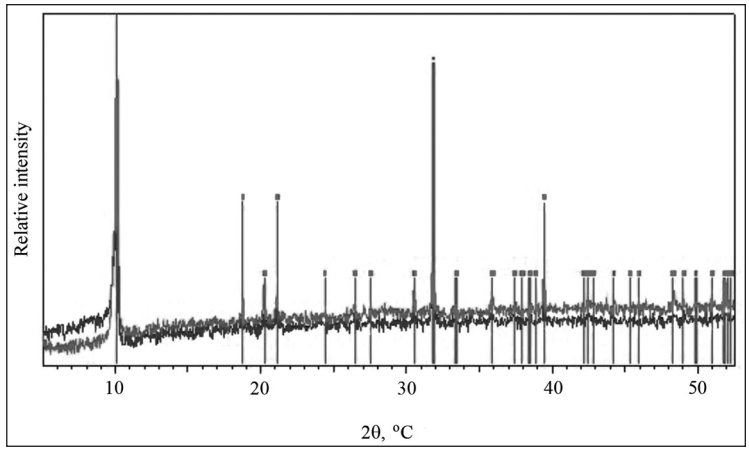

Fig. 1. X-ray diffraction patterns of $CoNH_4PO_4 \cdot H_2O$: synthesized (bottom), from Kremer Pigmente (top), and PDF [21–793] (vertical lines)

These results are almost consistent with those observed by IR measurements. The IR spectra of both samples are qualitatively identical regardless of their preparation history. The IR spectra of the synthesized pigment samples and those obtained from Kremer Pigmente are presented in Fig. 2.

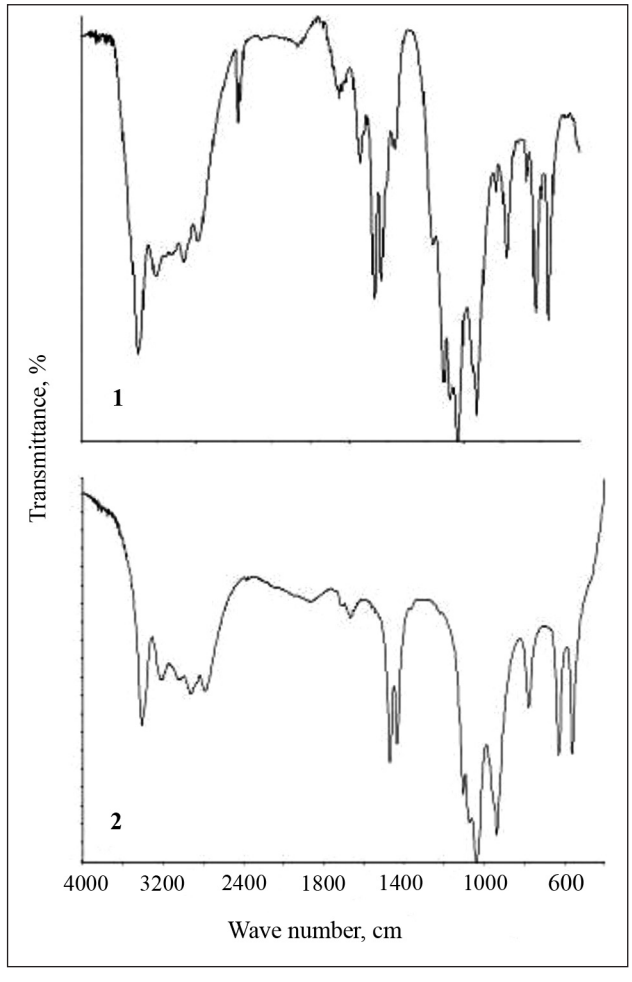

Fig. 2. IR spectra recorded for $CoNH_4PO_4 \cdot H_2O$ pigment samples: synthesized (1), from Kremer Pigmente (2)

A distinctive feature observed in both spectra of the pigment samples is absorption around 3400 cm^{-1} (strong) and 1660 cm^{-1} (weak), indicating the presence of crystallization water [13]. A number of strong and multiple absorptions in the range of 3220–2775 cm^{-1} and at 1469, 1431, 781 cm^{-1} could be attributed to the characteristic vibrations in NH_4^+. The absorption bands attributable to the characteristic P–O vibrations in the phosphate are clearly seen at 1103–937 cm^{-1} and 625–561 cm^{-1} [13–16].

The optical properties for both $CoNH_4PO_4 \cdot H_2O$ samples were also recorded. The optical reflection spectra were measured at room temperature in the range 400–700 nm. Figure 3 demonstrates the reflection spectra of two pigment samples. One can see that the reflection spectra are qualitatively almost identical (Fig. 3). In the beginning, the pigment samples show a wavelength-independent reflectance (from 400 nm up to ~445 nm, and up to ~430 nm for synthesized and Kremer Pigmente samples, respectively). From this point, a significant increase of reflection up to ~525 nm is seen. Starting from ~525 nm, the reflection abruptly decreases and again increases starting from ~555 nm. In the higher wavelength region (from ~650 nm), the reflection is almost constant, i. e. not wavelength-dependent, and close to unity, proving a high optical quality of the samples [15, 17].

Interestingly, an almost identical surface microstructure and particle size were observed for both pigment samples (Figs. 4 and 5). In both cases, the plate-like particles are seen with a very well pronounced agglomeration, indicating a good connectivity among the grains. Moreover, it is clear that a micrograin network is also formed. The SEM micrograph suggests that the

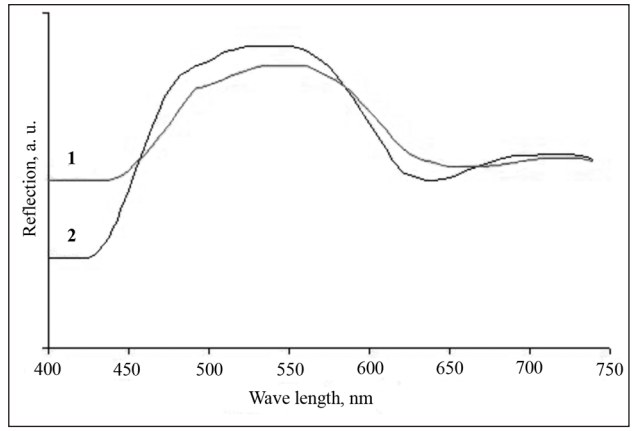

Fig. 3. The reflection spectra of $CoNH_4PO_4 \cdot H_2O$ pigment samples: synthesized (1), from Kremer Pigmente (2)

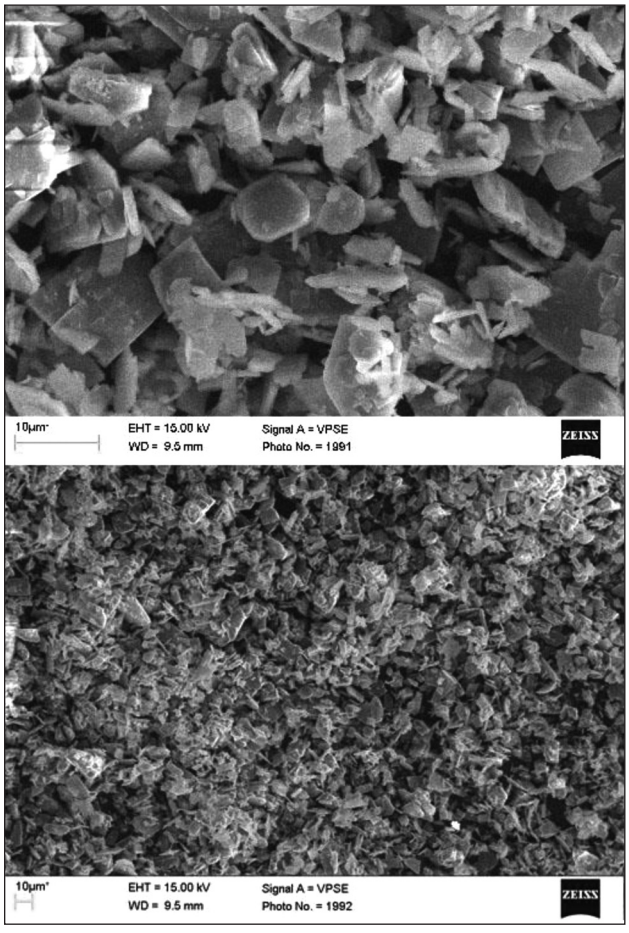

Fig. 4. SEM micrographs of the $CoNH_4PO_4 \cdot H_2O$ pigment synthesized by co-precipitation, obtained at two magnifications

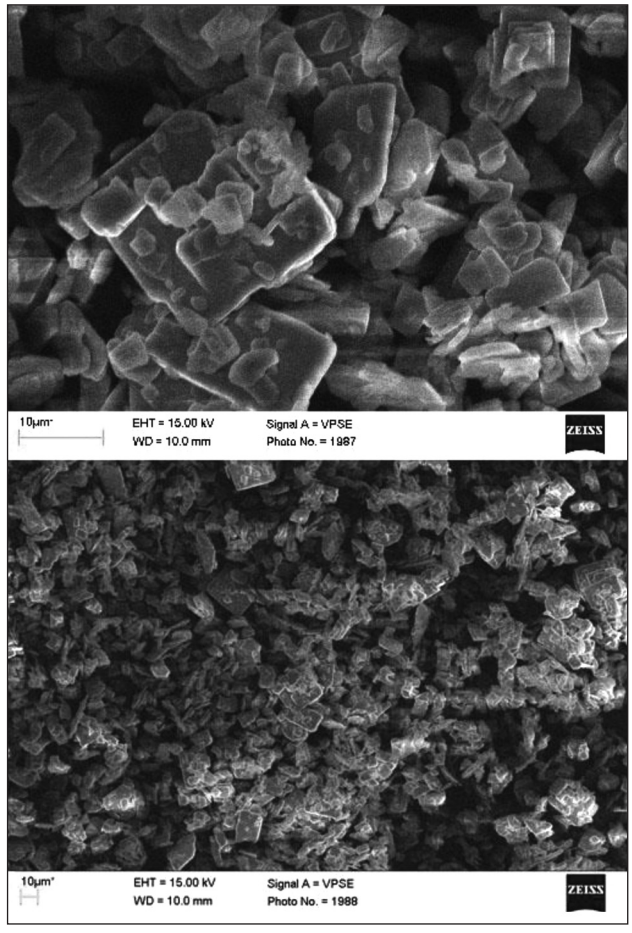

Fig. 5. SEM micrographs of the $CoNH_4PO_4 \cdot H_2O$ pigment from Kremer Pigmente, obtained at two magnifications

$CoNH_4PO_4 \cdot H_2O$ solids synthesized by co-precipitation (Fig. 4) are composed of irregular submicron grains of the average size less than 5 μm. Besides, the SEM image of the material prepared by co-precipitation exhibits a denser packing of smaller individual particles. In the case of the $CoNH_4PO_4 \cdot H_2O$ sample purchased from Kremer Pigmente (Fig. 5), formation of plate-like ultrafine crystallites of the average grain size ~3–12 μm is evident. As is seen, the adjacent grains tend to fuse, and the microscopic crystal growth on each grain begins to occur.

CONCLUSIONS

A cobalt light-violet pigment ($CoNH_4PO_4 \cdot H_2O$) has been prepared by the co-precipitation method. The characteristics of the obtained product were compared with those of a commercial sample purchased from Kremer Pigmente (Germany). The formation of a monophasic cobalt light-violet pigment by the co-precipitation method was confirmed by XRD analysis data. The optical reflection spectra proved the high optical quality of the samples. The SEM micrographs suggest that the $CoNH_4PO_4 \cdot H_2O$ solids synthesized by co-precipitation are composed of irregular submicron grains with the average grain size less than 5 μm.

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$CoNH_4PO_4$ PIGMENTO SINTEZĖ BENDROJO NUSODINIMO METODU

Santrauka

Kobalto šviesiai violetiniam pigmentui ($CoNH_4PO_4 \cdot H_2O$) sintetinti šiame darbe pasiūlytas paprastas bendrojo nusodinimo metodas. Susintetinto produkto savybės palygintos su komercinio produkto (Kremer Pigmente, Vokietija) analogiškomis savybėmis. Pigmentų pavyzdžiai apibūdinti Rentgeno spindulių difrakcinės analizės (XRD) ir infraraudonosios spektroskopijos (IR) metodais bei skleidžiamąja elektronine mikroskopija (SEM). Taip pat ištirtos abiejų $CoNH_4PO_4 \cdot H_2O$ pavyzdžių optinės savybės. Vienfazio kobalto šviesiai violetinio pigmento susidarymas bendrojo nusodinimo metodu patvirtintas XRD analizės duomenimis. Iš SEM nuotraukų padaryta išvada, kad bendrojo nusodinimo metodu susintetintas $CoNH_4PO_4 \cdot H_2O$ yra sudarytas iš nereguliarios formos submikroninių, mažesnių nei 5 μm kristalitų.