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SYNTHESIS AND CHARACTERIZATION OF NEWBERYITE

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Phosphates belong to the extensive group of inorganic pigments that are very often used in industry of plastics and anticorrosive paints. Also, the powders of newberyite $MgHPO_4{\cdot}3H_2O$ and α-pyrophosphate $Mg_2P_2O_7$ can find the usage in this field. Thus, these compounds were the centre of our attention. Newberyite and α-pyrophosphate were synthesized by the method of gelling. Impact of various ways of synthesis, especially reaction conditions, on the structural, thermal, physical and optical properties was investigated. α-pyrophosphate was synthesized by the thermal decomposition of newberyite at temperature around 500°C. Both powders are white color, but the newberyite is the whitest one. The reaction pH particularly affected the particle size distribution and optical properties.

Keywords: *magnesium pyrophosphate, newberyite, optical properties, pigments,* α*-pyrophosphate*

Introduction

Different phosphate compounds are widely used in several fields of industry, for example in agricultural, pharmaceutical, food, textile industry, etc. [1, 2]. The applications of the phosphates depend on their properties and at the same time their properties depend on the particular synthetic procedure used [2–4]. Many of metal phosphates are used as heterogeneous catalysts for a variety of organic processes [5]. Among them, the phosphates are also used as anticorrosive inorganic pigments because their main properties are insolubility in water, high temperature resistance and chemical stability [6]. The advantage of this type of compounds is the absence of ecologically (toxicologically) harmful elements. Our research group has been focused on synthesis of metal phosphates as the anticorrosive pigments for many years [7, 8].

The main aim of this work was to study the influence of synthetic procedure of newberyite $MgHPO_4{\cdot}3H_2O$ on the quantity of crystalline water, structure and its pigment-application properties. Thermal decomposition of newberyite and forming temperature of α-pyrophosphate were studied by thermoanalytical measurement.

Experimental

Materials

Solids of newberyite were prepared by gelling from magnesium hydroxide and orthophosphoric acid in various ambient conditions. The pH of reaction medium was changed by aqueous solution of sodium hydroxide (c=3 mol L^{-1}). Amount of starting raw materials $Mg(OH)_2$ (Acros, 31572; 95%) and H_3PO_4 (Lachema; 85% PA) was calculated on the basis of stoichiometry. The synthetic procedure is described below.

$$Mg(OH)_2+H_3PO_4+H_2O\xrightarrow{NaOH}MgHPO_4{\cdot}3H_2O$$

A suspension of $Mg(OH)_2$ in distilled water was immersed in an ice bath (drift ice). During the intensive stirring the concentrated orthophosphoric acid was slowly added by drops into the suspension of $Mg(OH)_2$. The pH of the reaction was changed by adding of 3 M NaOH from 0 to 6 mL (Table 1). The mixture was intensively stirred next 40 min but within few minutes of stirring the gel started to arise. Then the gel was allowed to stand for 24 h, filtered and suspended in distilled water (20 mL g^{-1} of solid). After 30 min of stirring in an ice bath, it was allowed to stand for 24 h, filtered, air dried and analyzed.

Table 1 The synthetic variables and nomenclature of newberyite samples prepared

Sample	NaOH/mL	pH
newb. 1	0	5.80
newb. 2	1	7.39
newb. 3	2	8.45
newb. 4	3	8.53
newb. 5	4	8.55
newb. 6	5	8.57
newb. 7	6	8.60

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Methods

The quantity of crystalline water was counted on the basis of mass loss during thermoanalytical measurement. Simultaneous TG/DTA measurements were performed by STA Jupiter 449 equipment (Netzsch GmbH, Germany) in the temperature range 50–600°C at heating rate 10°C min^{-1}. The analysis was carried out in a ceramic crucible under air and α-Al_2O_3 was used as a reference material.

The X-ray diffractograms of the samples of newberyite in the range 2θ of 10–80° were obtained using the diffractometer D8 (Bruker, GB), CuK_α radiation, scintillation detector.

The solids obtained after the thermoanalytical measurement (burnout at 600°C) were analyzed by energy-dispersive X-ray analysis (EDAX) by equipment of JEOL JSM-5500LV (JEOL Inc., USA) with IXRF system and GRESHAM Sirius 10 detector. The EDAX analysis provided the percentage elemental compositions of the solids $Mg_2P_2O_7$. The composition of solid is compared with the theoretical values and with the values obtained from bibliography [3].

The particle size distribution of the samples was measured by equipment of Mastersizer 2000/MU (Malvern Instruments, UK). It is a highly integrated laser measuring system for analysis of particle size distribution. The equipment uses the scattering of incident light on particles. The solids were measured in ethanol medium. The signal was evaluated on the basis of Fraunhofer bending.

The colour properties of the solid samples were measured in absorption cells. Colour properties were measured in the visible region (400–700 nm) with Color Quest XE (Hunter Lab, USA). The measurement conditions were following: Illuminant D65 (6500 K), 10° complementary observer and geometry of measurements $d/8°$, colour space CIE $L^*a^*b^*$. The color coordinate L^* describes brightness. The color coordinate a^* reflects amount of green (–) and red (+) hue. The color coordinate b^* means reflects amount of blue (–) and yellow (+) hue. Total colour difference ΔE^*_{CIE} represents the differences between compared samples and standard. The total colour difference was calculated according to an equation below.

$$\Delta E^*_{\text{CIE}} = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}}$$

where
$\Delta L^{*2} = L^*_{\text{std}} - L^*_{\text{sample}}$; $\Delta a^{*2} = a^*_{\text{std}} - a^*_{\text{sample}}$; $\Delta b^{*2} = b^*_{\text{std}} - b^*_{\text{sample}}$

Results and discussion

The synthetic variables and nomenclature of the newberyite samples prepared are summarized in Table 1. The pH of reaction was changed in range of pH values 5.8–8.6. Results of the thermoanalytical measurements of all samples of newberyite were very similar and therefore Fig. 1 can be used for characterisation of thermal decomposition of all samples. Figure 1 presents the TG and DTA curves of the newb. 3.

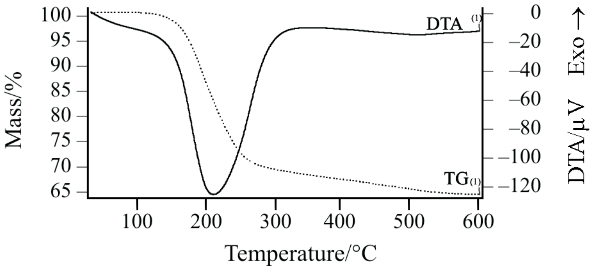

Fig. 1 DTA and TG curves of the thermal decomposition of newb. 3 (sample mass 183.70 mg)

Table 2 Thermal characteristics and quantity of crystalline water of newberyites prepared

Sample	Temperature range/°C	Peak temperature/°C	Partial mass loss/%	Total mass loss/%	Quantity of crystalline water
newb.1	140–330 330–600	214 –	30.02 5.44	35.46	2.93
newb.2	135–300 300–500	212 –	29.02 3.93	33.73	2.77
newb.3	140–320 320–600	212 509	31.49 4.36	35.93	2.98
newb.4	140–300 300–600	219 435	30.04 5.93	35.97	2.98
newb.5	140–320 320–600	218 –	32.72 3.88	36.60	3.04
newb.6	140–300 300–600	216 504	31.45 5.32	36.77	3.06
newb.7	140–300 300–600	218 –	31.75 5.09	36.84	3.07

The endothermic peak with minimum at temperature 212°C corresponds to the loss of crystalline water. The endothermic process started at temperature around 140°C. The mass defect 31.49% is connected with the loss of 3 molecules of crystalline water. The next mass loss 4.36% corresponds to the condensation of 1/2 of constitution water. This process starts around of temperature 320°C (TG curve) and it is noticeable also on DTA curve where slight endothermic peak with minimum at 509°C is. The total mass loss 35.93% corresponds to the loss of 2.98 molecules of crystalline water of newb. 3. In some cases (newb. 1, 2, 5, 7) the second endothermic peak that characterised the creation of α-pyrophosphate was not detected at DTA curve. Theoretical total mass loss for $MgHPO_4{\cdot}3H_2O$ is 36.16%. The differences between quantities of crystalline water of constituent samples of newberyite are minimal (Table 2) thus we can state that the pH of reaction does not affect this characteristic of newberyite. Thermal decomposition of $MgHPO_4{\cdot}3H_2O$ and creation of α-pyrophosphate $Mg_2P_2O_7$ are described by two partial and one total reaction equations below.

The first partial reaction (140–320°C)

$$2MgHPO_4{\cdot}3H_2O \rightarrow 2MgHPO_4+6H_2O$$

The second partial reaction (320–600°C)

$$2MgHPO_4 \rightarrow Mg_2P_2O_7+H_2O$$

Total reaction (140–600°C)

$$2MgHPO_4{\cdot}3H_2O \rightarrow Mg_2P_2O_7+6H_2O$$

The prepared samples were subjected to X-ray diffraction analysis. All samples were identified as one-phase system of newberyite (Fig. 2). Newberyite has orthorhombic crystal structure. The difference between samples was in values of lattice parameters. The sample of newb. 1 prepared at the lowest reaction pH (pH=5.8) was identified as $MgHPO_4{\cdot}3H_2O$, syn (JCPDS 35-0780) with values of a=1.02083, b=1.06845 and c=1.00129 nm. The increase of reaction pH to 7.4 caused the formation of $MgHPO_4{\cdot}3H_2O$ (JCPDS 72-0023) with values of a=1.0215, b=1.0681 and c=1.0014 nm. The pH of reaction higher than 8 produced the formation of newberyite, syn ((JCPDS 70-2345) where a=1.0203, b=1.0678 and c=1.0015 nm.

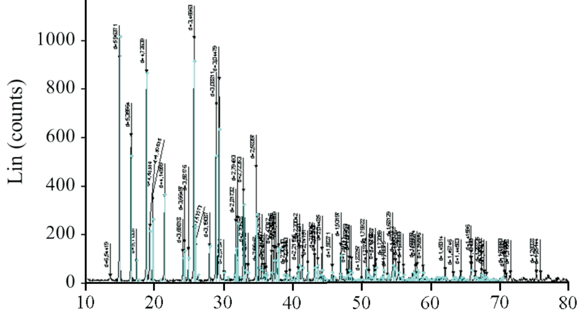

Fig. 2 X-ray diffraction pattern of newb. 3

Table 3 Elemental composition of solids α-pyrophosphate $Mg_2P_2O_7$

Sample	Mg/at%	P/at%	O/at%
α-pyrophosphate 1	18.6	20.7	60.7
α-pyrophosphate 2	19.1	21.6	59.3
α-pyrophosphate 3	22.5	19.3	58.2
theoretical	18.2	18.2	63.6
bibliography [3]	16.4	14.2	69.3

The solids of α-pyrophosphate obtained from thermoanalytical measurement of newberyite (T=600°C) were analyzed by EDAX. The EDAX analysis of the solid provided the percentage elemental compositions given in Table 3. The composition of solid is compared with the theoretical values and with the values acquired from bibliography [3]. The main task of the analysis was to testify whether the residuals of sodium cation did not build in the crystal lattice of newberyite and therefore in the crystal lattice of α-pyrophosphate. This assumption was confirmed. The differences in elemental composition between samples prepared and theoretical values are the most probably caused by difficulty of preparation pure magnesium phosphate – newberyite $MgHPO_4{\cdot}3H_2O$. Small amount of no crystalline sodium-magnesium mixed orthophosphates and other magnesium orthophosphates are the most often formed during reaction. These compounds are partially soluble in water and therefore the washing was reflected in compositional changes.

From the pigmentary point of view it is necessary to characterize newberyite and α-pyrophosphate samples by analysis of particle size distribution and also to define colour properties. Colour properties of the newberyite samples are described in Table 4. The powders have white colour but the colour hues of all samples are slightly shifted to the blue field of colour space CIE $L^*a^*b^*$. Colour coordinate a^* of sample newb. 2 is located in red, the other samples contained minimum amount of green hue. Sample

Table 4 Colour properties of newberyite samples

Sample	L^*	a^*	b^*	ΔE^*_{CIE}
newb. 1	94.28	–0.23	1.94	–
newb. 2	93.42	0.37	2.18	0.89
newb. 3	93.32	–0.03	1.84	0.84
newb. 4	93.77	–0.02	2.28	0.37
newb. 5	94.04	–0.27	2.21	0.36
newb. 6	93.69	–0.14	2.19	0.37
newb. 7	93.77	–0.15	1.86	0.46

Table 5 Colour properties of α-pyrophosphate $Mg_2P_2O_7$ samples

Sample	L^*	a^*	b^*	ΔE^*_{CIE}
α–pyrophosphate 1	82.86	0.25	3.48	–
α–pyrophosphate 2	88.32	0.01	2.55	5.55
α–pyrophosphate 3	90.46	0.07	2.07	7.68
α–pyrophosphate 4	87.17	0.02	2.57	4.42
α–pyrophosphate 5	87.81	0.00	2.49	5.06
α–pyrophosphate 6	87.37	0.10	2.81	4.56
α–pyrophosphate 7	87.56	0.04	2.64	4.78

Table 6 Particle size distribution of newberyite samples

Sample	main particle size d_{50}/μm	range of particle sizes d_{10}–d_{90}/μm	specific surface area a/m^2 g^{-1}
newb. 1	15.02	2.89–41.94	0.91
newb. 2	30.96	2.70–89.90	0.85
newb. 3	27.76	14.17–44.24	0.51
newb. 4	40.70	7.53–87.02	0.46
newb. 5	48.90	15.39–96.77	0.32
newb. 6	49.70	16.96–98.81	0.37
newb. 7	56.18	9.49–108.25	0.38

newberyite 1 is the lightest and the whitest one although the colour differences between this sample (std.) and the others are almost indistinguishable for the human eyesight. Thus, the pH of reaction does not affect the colour properties of the samples and if so, this affect is very small and immaterial.

The different situation arose in case of α-pyrophosphate (Table 5). Newb. 1 prepared without presence of NaOH is the darkest sample, it means that this sample have the lowest value of coordinate L^*–brightness. The presence of NaOH in reaction mixture affected all colour coordinates. Sample newb. 1 contains the biggest amount of red and yellow hue. The total colour difference between newb. 1 and the others is considerable and differentiable by human eyesight. Samples have white-grey colour.

The presence of NaOH has big affect on the particle size distribution (Table 6). The solid prepared at pH of reaction less than 6 has the main size d_{50}=15 μm. The increasing of reaction pH caused also the increasing of main particle size of newberyite samples up to values d_{50}=50 μm. For the usage of the samples as inorganic pigments the main particle size has to be reduced by milling on the values less than 10 μm. The laser measuring equipment Mastersizer 2000/MU also provided the values of specific surface area of the samples measured. However, these values have only an orientation meaning. The influence of increasing reaction pH on values of specific surface area of the samples has declining character.

Conclusions

In the presented work the influence of various reaction pH of synthesis on the quantity of crystalline water of newberyite, structure, physical and optical properties was investigated. The quantities of crystalline water of newberyite ($MgHPO_4 \cdot 3H_2O$) were determined by thermoanalytical measurement. The significant affect of reaction pH was not found out. The products of thermoanalytical measurement (600°C) – α-pyrophosphates ($Mg_2P_2O_7$) were analysed by EDAX analysis. Residuals of sodium cation were not built in the crystal lattice of α-pyrophosphate. The reaction pH slightly affected the particle size distribution and also the specific surface area. The increasing values of pH caused the growth of particle size distribution and decrease of the specific surface area.

Prepared samples of newberyite have white colour and the affect of reaction pH on the colour properties was not found out. Samples of α-pyrophosphates are also white, but the colour is darker than colour of newberyites. Reaction pH affects the colour of α-pyrophosphates considerable; sample 1 (pH=5.8) is almost light grey while the other samples (pH=7.4–8.6) are white.

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