ELSEVIER

Dyes and Pigments 44 (2000) 161–164

DYES and PIGMENTS

The synthesis of binary zinc(II)–nickel(II) cyclo-tetraphosphates as new special pigments

Miroslav Trojan*, Petra Šulcová, Petr Mošner

Department of Inorganic Technology, Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, Legions Sq. 565, 532 10 Pardubice, Czech Republic

Received 28 February 1999; accepted 23 August 1999

Abstract

The synthesis of new inorganic pigments has been investigated, with the goal of preparing heat stable and anticorrosive pigments. The synthesis of the title pigments is based on temperature calcination of the starting materials, and the optimum reaction conditions for this process have been assessed. The pigments have been evaluated from the standpoint of their structure, colour hue and ability to dye ceramic glazes. New binary condensed phosphates were synthesised based on results of thermal analyses. These new compounds were developed with environmentally friendly special pigments in mind.

Keywords: Binary tetraphosphates; Zinc; Nickel (II); Special pigments

1. Introduction

The increasing need for pigments, the desire for new interesting pigment colours, and the fact that many pigments contain toxic elements (e.g. Pb, Cr, Sb, Cd, Se), has opened the door to the development of new environmentally friendly pigments [1]. For this reason the focus of our studies has been the preparation of pigments that would meet the demands of modern-day colorants [2]. In view of existing needs, the goal of this work was to identify new compounds that could be used as special thermostable pigments with anticorrosion-inhibition properties. Binary zinc(II)–nickel(II) tetraphosphates with cyclic anions have not been described in literature so far [3]. In view of this observation, cyclo-tetraphosphates of selected divalent metals were prepared in our laboratory and examined for their utility as special inorganic pigments.

2. Experimental

The procedure used to prepare mixed cyclo-tetraphosphates is a two-step process. In the first step (Scheme 1), a mixture of pure cyclo-tetraphosphates containing bivalent metals is melted (30 min) in air and then cooled abruptly to give an amorphous product composed of higher linear phosphates of the formula $(Zn_{2-x}Ni_x)_{n/4}H_2P_nO_{3n+1}$. In the second step (Scheme 2) this product is heated repeatedly to a suitable temperature and

* Corresponding author. Fax: +420-40-603-7275.
E-mail address: miroslav.trojan@upce.cz (M. Trojan).

0143-7208/00/$ - see front matter
PII: S0143-7208(99)00091-1

recrystallized to give a microcrystalline product ($Zn_{2-x}Ni_xP_4O_{12}$ where $x = 0$, 0.25, 0.50, 0.75, 1.00, 1.25, 1.50, 1.75 and 2. This chemistry gave the binary cyclo-tetraphosphates of the summary formula $Zn_{2-x}Ni_xP_4O_{12}$, where $x = 0.25$, 0.50, 0.75, 1.00, 1.25, 1.50 and 1.75, as well as pure $Zn_2P_4O_{12}$ ($x = 0$) and pure $Ni_2P_4O_{12}$ ($x = 2$) pigments.

The mixtures were formed in platinum dishes in an electric furnace, by heating starting cyclo-tetraphosphate ($Ni_2P_4O_{12}$) above 1250°C. After 30 min, dishes containing the molten products were removed from the furnace and cooled abruptly by immersion in water. The vitreous products ($(Zn_{2-x}Ni_x)_{n/4}H_2P_nO_{3n+1}$) obtained were dried at 150°C and ground in a vibrating pebble mill. Various portions of these intermediates were then subjected to DTA (Perkin–Elmer DTA 1700) in order to determine the temperatures for thermal recrystallization (T_{Ri} and T_{max}).

The individual intermediates ($(Zn_{2-x}Ni_x)_{n/4}H_2PnO_{3n+1}$) were then calcinated in an electric resistance furnace at 50°C above (T_{max}) for 30 min. The sintered blocks of the final products ($Zn_{2-x}Ni_xP_4O_{12}$) were ground in the vibrating pebble mill, and the yields were determined by using a special extraction method [4]. Extraction of the calcinates with 0.3 M HCl made it possible to determine the temperature ranges at which the individual intermediates existed [5,6] and the degree of conversation of the calcinates to the final products.

The starting cyclo-tetraphosphates, vitreous amorphous intermediates, and final products (binary cyclo-tetraphosphates) were analysed by X-ray powder diffraction. (Cu K_α, $\lambda = 0.154178$ nm, HZG-4B apparatus, Germany). The diffractograms were indexed under the assumption that the mixed cyclo-tetraphosphates were isostructural with $Zn_2P_4O_{12}$ and $Ni_2P_4O_{12}$ [7]. The lattice parameters of the monoclinic unit cell (C2c space group) were calculated by least squares treatment.

The products were analysed using pycnometrical method to estimate their density and by the DTA method combined with high-temperature microscopy (MHO-2, Zeiss Jena) to estimate their melting temperatures.

3. Results and discussion

The main goal of present work was to develop conditions for the synthesis of mixed cyclo-tetraphosphates of the type $Zn_{2-x}Ni_xP_4O_{12}$. The starting cyclo-tetraphosphates ($Zn_2P_4O_{12}$, $Ni_2P_4O_{12}$) were prepared by the thermal method described in Ref. [8]. In our laboratory this procedure was modified to obtain the purest possible products. The synthesis of the cyclo-tetraphosphates is outlined in Scheme 1 where M^{II} = Zn, Ni, and $p(H_2O) = 100$ kPa.

The synthesis of the mixed cyclo-tetraphosphates was carried out according to Scheme 2.

The temperatures (T_{Ri} and T_{max}) of recrystallization, as a function of increasing nickel content are listed in reaction yields are also presented in Table 1.

$$M^{II}CO_3 + 2\,H_3PO_4 \rightarrow M(H_2PO_4)_2 + H_2O + CO_2 \quad (170°C)$$

$$M(H_2PO_4)_2 \rightarrow MH_2P_2O_7 + H_2O \quad (260°C)$$

$$MH_2P_2O_7 \rightarrow M_2P_4O_{12} + H_2O \quad (325°C)$$

Scheme 1. Three-stage synthesis of cyclo-tetraphosphate pigments.

$$(1 - x/2)\,Zn_2P_4O_{12} + x/2\ Ni_2P_4O_{12} + 4/n\ H_2O \rightarrow 4/n\,(Zn_{2-x}Ni_x)_{n/4}H_2P_nO_{3n+1}\ (l) \quad (1260°C, \text{melting in air})$$

$$4/n(Zn_{2-x}Ni_x)_{n/4}H_2P_nO_{3n+1}\ (l) \rightarrow (Zn_{2-x}Ni_x)_{n/4}H_2P_nO_{3n+1}\ (\text{glass}) \quad (1260 - 25°C, \text{solidification})$$

$$(Zn_{2-x}Ni_x)_{n/4}H_2P_nO_{3n+1}\ (\text{glass}) \rightarrow 4/n\ H_2O + Zn_{2-x}Ni_xP_4O_{12}\ (\text{cryst.}) \quad (T_{Ri}, \text{recrystallization})$$

Scheme 2. Three-stage preparation of mixed cyclo-tetraphosphate pigments.

Table 1
Experimental data for $Zn_{2-x}Ni_xP_4O_{12}$ pigments

x	T_{Ri} (°C)	T_{max} (°C)	Yield (%)
0.00	545	573	90.5
0.25	555	585	91.2
0.50	570	605	92.0
0.75	590	625	92.8
1.00	615	655	93.6
1.25	650	690	94.5
1.50	690	725	95.7
1.75	730	760	97.2
2.00	776	796	98.6

Table 3
Melting temperatures and densities for $Zn_{2-x}Ni_xP_4O_{12}$ pigments

x	T_{melt} (°C)	$Density_{calc.}$ (g cm^{-3})	$Density_{exp.}$ (g cm^{-3})
0.00	810	3.493	3.50
0.25	820	3.509	3.51
0.50	840	3.515	3.51
0.75	875	3.513	3.51
1.00	920	3.511	3.51
1.25	975	3.500	3.50
1.50	1050	3.491	3.49
1.75	1145	3.481	3.48
2.00	1250	3.480	3.48

The yields were high and increased with increased nickel content. The $P_2O_5/(Zn+Ni)$ molar ratio in the 0.3 M HCl extracted products varied from 0.9980 to 1.0018. The Zn/Ni: molar ratio corresponds to the $(2-x)/x$ values in Table 2. Products were found to a single phase containing cyclo-tetraphosphate anions, specifically a mixed zinc(II)–nickel(II) cyclo-tetraphosphate ($Zn_{2-x}Ni_xP_4O_{12}$) in the whole region of [$x[x \in (0, 2)$].

The structural parameters of $Zn_{2-x}Ni_xP_4O_{12}$ (Table 2) were limited by those associated with $Zn_2P_4O_{12}$ and $Ni_2P_4O_{12}$. The volume of the unit cell decreased slightly with increasing nickel content, which were consistent with the fact that the ionic radius of nickel(II) is slightly smaller than zinc(II).

Some physical properties of the title pigments are summarized in Table 3. The section of DTA curves above the melting temperature can be used to estimate the thermal stabilities of the mixed cyclo-tetraphosphates. The endothermic effects observed in DTA curves, along with high-temperature microscopy, were used to establish T_{melt}. Cyclo-tetraphosphates formation was favoured by the presence of at least traces of water vapour in the air atmosphere, and occured according to Scheme 3. Under these conditions the melting temperatures represent the temperatures up to which the mixed cyclo-tetryphosphates are stable. By increasing nickel content, T_{melt} increased from 810 to 1250°C. This behavior extends the scope of their use to high-temperature application. We also found that the densities of the mixed zinc(II)–nickel(II) cyclo-tetraphosphates differed very little as x was increased.

When the effect of increasing nickel content on pigment colour was assessed, the intensity of pigment colour was found to increase with increasing

$$Zn_{2-x}Ni_xP_4O_{12}\ \text{(cryst.)} + 4/n\ H_2O\ \text{(g)} \rightarrow 4/n(Zn_{2-x}Ni_x)_{n/4}H_2P_nO_{3n+1}\ \text{(l)}$$

Scheme 3. The contribution of water to cyclo-tetraphosphate formation.

Table 2
Structural parameters for $Zn_{2-x}Ni_xP_4O_{12}$ pigments

x	a (nm)	b (nm)	c (nm)	β (°)	V (nm^3)
0.00	1.1778(5)	0.8305(4)	0.9910(4)	118.83(3)	0.8492
0.25	1.1733(3)	0.8291(3)	0.9873(4)	118.72(2)	0.8423
0.50	1.1703(6)	0.8287(4)	0.9842(4)	118.63(3)	0.8378
0.75	1.1692(5)	0.8275(4)	0.9836(4)	118.66(2)	0.8351
1.00	1.1673(5)	0.8265(4)	0.9840(4)	118.62(2)	0.8324
1.25	1.1666(4)	0.8262(3)	0.9836(4)	118.60(2)	0.8323
1.50	1.1656(4)	0.8246(3)	0.9841(4)	118.57(2)	0.8308
1.75	1.1649(2)	0.8247(3)	0.9837(4)	118.56(1)	0.8300
2.00	1.1644(5)	0.8238(3)	0.9813(4)	118.53(3)	0.8270

nickel content. Based on colour measurements (CIEL*a*b*) conducted on pigment powders, it was also found that increasing nickel content changed pigment colour from intense yellow to intense yellow-green.

4. Conclusions

Cyclo-tetraphosphates of type $Zn_{2-x}Ni_xP_4O_{12}$ have been synthetised as new inorganic pigments. The products crystallized in the monoclinic system, C2c. New binary condensed phosphates were synthesised with the aide of results from thermal analysis, and these new compounds are proposed as environmentally friendly pigments.

The binary products containing higher nickel content possessed interesting yellow or yellow–green colours, and can be classified as high-temperature pigments that are based on condensed phosphates. The synthesis of these pigments is based on a reversible process that was detected using thermal analysis.

References

[1] Trojan M, Šulcová P. The development of new environmentally friendly pigments using methods of thermal synthesis. Proc. 7th Polish Seminar in Memory of Bretsznajder, Plock, 1998. p. 28–34.
[2] Trojan M, Šolc Z, Novotny M. Pigments, Kirk–Othmer encyclopedia of chem. pigments, technol., vol. 17. New York: J. Wiley and Sons Inc, 1995.
[3] Trojan M, Beneš L. Mat Res Bull 1991;26:693.
[4] Trojan M, Brandová D. Thermochim Acta 1986;80:541.
[5] Trojan M, Brandová D. Czech Patent 232 090, 1984.
[6] Trojan M. Chem Listy 1986;80:541.
[7] Begieu-Beucher M, Codrand M, Perroux M. J Solid State Chem 1976;19:359.
[8] Thilo E, Grunze H. Z Anorg Allg Chem 1957;280:209.