Journal of Thermal Analysis and Calorimetry, Vol. 68 (2002) 75–79

THERMAL ANALYSIS OF Ba(II)–Sr(II) CYCLO-TETRAPHOSPHATES(V)

M. Trojan, P. Šulcová and L. Sýkorová

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

Abstract

The synthesis of new inorganic pigments has been investigated with the goal of preparing heat stable and anticorrosive pigments. The synthesis is based on a thermal procedure making use of the reversible transformation of cyclo-tetraphosphates(V) to higher linear phosphates(V). New binary condensed phosphates were synthesized based on the results of thermal analysis. These compounds represent new environmentally-friendly special pigments.

Keywords: anticorrosive pigments, condensed phosphates(V), cyclo-tetraphosphates(V)

Introduction

Binary Ba(II)–Cr(II) cyclo-tetraphosphates(V) have been synthesized as new binary compounds. The synthesis is based on a thermal procedure making use of the reversible transformation of cyclo-tetraphosphates(V) to higher linear phosphates [1]. With respect to the proposed application of these products as special inorganic pigments some properties (thermal stability, structural parameters, anticorrosion activity) have been determined.

Binary (mixed) cyclo-tetraphosphates(V) of the *c*-$Ba_{2-x}Sr_xP_4O_{12}$ type have been prepared in our laboratory as new thermally stable anticorrosive pigments [1]. From the point of view of application the combination of Ba and Sr cations in these compounds appears very advantageous. Their synthesis is based on two types of thermal methods.

Experimental

Two methods of preparation of condensed phosphates(V) can be used for their synthesis. The first one consists in high-temperature calcination. This procedure is based on a two-step thermal synthesis. The first step, starting from the compounds of the bivalent metals, involves their melting in air atmosphere and then abruptly cooling to give a vitreous amorphous product [2] composed of higher linear phosphates. In the second step this product is repeatedly heated to a suitable temperature and

1418–2874/2002/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

recrystallized in order, to give a microcrystalline product. On the basis of this method new high-temperature pigments have been prepared.

The second method of preparation, which is called middle temperature synthesis, is based on the thermal dehydration of a useful compound or a mixture of dihydrogenphosphates [3]. The main aim is to find such compounds that can be used as special thermostable pigments with anticorrosion-inhibition properties.

The first method (high-temperature) was used to test the possibility of synthesis and determination of binary metaphosphate systems. Then we tested the second method of synthesis. Realisation of this method is easier (the high-temperatures are not used, corrosive melt of phosphates does not appear during synthesis). The products obtained by the second method are then tested for pigment application, especially, anticorrosion-inhibition properties.

The synthesis of the binary cyclo-tetraphosphates(V) by high-temperature methods is described in the following scheme:

$$(2-x)M^{II}_{A}O(CO_3)+xM^{II}_{B}O(CO_3)+4H_3PO_4 \rightarrow \\ \rightarrow 4/n(M_{A(2-x)}M_{B(x)})_{n/4}H_2P_nO_{3n+1}+(6-4/n)H_2O+(2CO_2) \quad (1)$$

$$4/n(M_{A(2-x)}M_{B(x)})_{n/4}H_2P_nO_{3n+1} \rightarrow 4/n(M_{A(2-x)}M_{B(x)})_{n/4}H_2P_nO_{3n+1} \quad (2)$$

(a vitreous product)

$$4/n(M_{A(2-x)}M_{B(x)})_{n/4}H_2P_nO_{3n+1} \rightarrow M_{A(2-x)}M_{B(x)}P_4O_{12}+4/nH_2O \quad (3)$$

(a microcrystal product)

Middle-temperature method was investigated for industrial commercialisation by our work place.

$$(2-x)M_AO(OH,CO_3)+xM_BO(OH,CO_3)+4H_3PO_4 \rightarrow \\ \rightarrow 2M_{A_{(1-x/2)}}M_{B_{(x/2)}}(H_2PO_4)_2+(H_2O)+(CO) \quad (4)$$

$$2M_{A_{(1-x/2)}}M_{(x/2)}(H_2PO_4)_2 \rightarrow 2Me_{A_{(1-x/2)}}M_{B_{(x/2)}}H_2P_2O_7+2H_2O \quad (5)$$

$$2Me_{A_{(1-x/2)}}M_{B_{(x/2)}}H_2P_2O_7\ (glass) \rightarrow 2H_2O+M_{A_{(2-x)}}M_{B_{(x)}}P_4O_{12}\ (cryst.) \quad (6)$$

The temperature region of the formation of these types of pigments was followed by thermal analysis using a Derivagtograph-C apparatus (MOM, Hungary) which allows the evaluation of data and simultaneous registration of the thermoanalytical curves TG, DTG and DTA. The thermal analysis provided the first information on the temperature region of the formation of the investigated pigments. The prepared starting mixtures were studied by thermal analysis in ceramic crucible in air. The increase of temperature was 5°C min^{-1}. α-Al_2O_3 was used as a heat-resistance standard.

The products were also evaluated by DTA and by high-temperature microscopy to estimate their melting temperatures [4].

Results and discussion

The methods of thermal analysis facilitate the detection and explanation of processes that accompany the melting of cyclo-tetraphosphates(V) and their recrystallization. An exothermic process was indicated by means of DTA [5]. This process represents the formation of the binary cyclo-tetraphosphate from intermediate higher linear phosphates and is connected with recrystallization of the amorphous vitreous phase.

The yields are high and increase with the increasing Sr content. Each product is a mono-phase material with a cyclo-tetraphosphate anion. Hence, the products (Table 1) are of the type of the binary Ba(II)–Sr(II) cyclo-tetraphosphates(V) of formula $Ba_{2-x}Sr_xP_4O_{12}$. This conclusion applies to the whole range of x. The pigment densities were determined by a standard procedure.

Table 1 Experimental data for the $Ba_{2-x}Sr_xP_4O_{12}$ pigments

x	T_{melt}/°C	$T_{recryst}$/°C	Yield/%	Density/g cm^{-3}
0	890	515	88.97	3.64
0.25	930	525	91.03	3.65
0.50	950	530	90.42	3.66
0.75	975	530	92.38	3.48
1.0	980	530	93.38	3.28
1.25	990	535	89.44	3.23
1.50	1000	535	93.32	3.18
1.75	1010	540	91.02	3.19
2.0	1020	570	90.81	3.18

As the yields of this synthesis were high, the intervals of DTA curves above recrystallization and melting temperature can be considered to indicate the thermal stabilities of the binary cyclo-tetraphosphates(V) (Table 1). The endothermic effects on DTA curves document melting (which was confirmed by means of high-temperature microscopy), which is incongruent. The cyclo-tetraphosphates are transformed into higher linear phosphates, which is favoured by the presence of at least traces of water vapour in air atmosphere [5].

Hence, in these conditions the melting temperatures represent the temperatures up to which the binary cyclo-tetraphosphates(V) are stable. The temperatures increase with the strontium content from 890 to 1020°C. This fact documents high thermal stability of the products that extends the range of their applications to high-temperature purposes [6].

The binary Ba(II)–Sr(II) cyclo-tetraphosphates(V) were colourless, which is advantageous for their application as special anticorrosive pigments of high thermal stability. The coatings containing these anticorrosive pigments may be easily coloured to the desired hue by means of cheaper classical pigments.

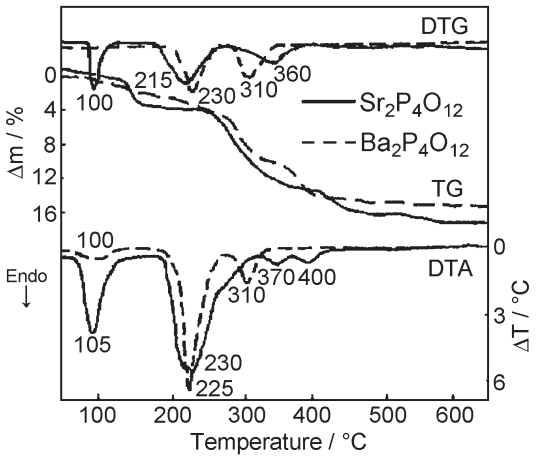

Fig. 1 Thermoanalytical curves for *c*-$Ba_2P_4O_{12}$ and *c*-$Sr_2P_4O_{12}$

The thermal analysis has been used to study the middle-temperatures synthesis of the binary cyclo-tetraphosphates. The thermoanalytical curves indicating formation of *c*-$Ba_2P_4O_{12}$ and *c*-$Sr_2P_4O_{12}$ are demonstrated in Fig. 1. The thermal analysis provided the first information on the temperature region of formation of this type of compounds.

Temperatures of recrystallization of all samples prepared (Table 1) were determined on the basis of results of thermal analysis. DTA curves of the vitreous intermediates indicating the formation of the microcrystalline products $Ba_2P_4O_{12}$ and $Sr_2P_4O_{12}$ show an exothermic effect (Fig. 2). From Fig. 2 it follows that the exothermic effect for $Sr_2P_4O_{12}$ is shifted to higher temperature (570°C) than in the case of $Ba_2P_4O_{12}$ (515°C). The exothermic effects of the mixed compounds are in this temperature range.

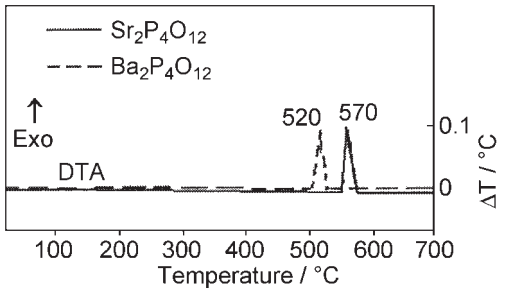

Fig. 2 DTA curves of the vitreous intermediates indicating the formation of the microcrystalline products: $Ba_2P_4O_{12}$ and $Sr_2P_4O_{12}$

Conclusions

The main attention was focused on the synthesis of the binary cyclo-tetraphosphates *c*-$Ba_{2-x}Sr_xP_4O_{12}$. Their application and anticorrosion-inhibition properties are followed. Some of these compounds are shown as new hopeful environmentally-friendly anticorrosive pigments, mainly *c*-$Ba_{1.25}Sr_{0.75}P_4O_{12}$, *c*-$Ba_{1.0}Sr_{1.0}P_4O_{12}$, *c*-$Ba_{0.75}Sr_{1.25}P_4O_{12}$, *c*-$Ba_{0.50}Sr_{1.50}P_4O_{12}$, *c*-$Ba_{0.25}Sr_{1.75}P_4O_{12}$. The binary products containing strontium seem to be interesting as to their anticorrosion properties. These pigments are environmentally-friendly and, therefore, very progressive, too.

References

1 M. Trojan, Dyes and Pigments, 13 (1990) 1.
2 M. Trojan, J. Mater. Sci., 25 (1990) 2159.
3 M. Trojan and D. Brandová, Thermochim. Acta, 157 (1990) 11.
4 J. Málek and J. Klikorka, J. Thermal Anal., 32 (1987) 1883.
5 M. Trojan and P. Šulcová, J. Therm. Anal. Cal., 60 (2000) 215.
6 M. Kurzawa and M. Bosacka, J. Therm. Anal. Cal., 56 (1999) 211.