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Binary Cyclotetraphosphates $Zn_{2-x}Ca_xP_4O_{12}$ as New Special Pigments

M. Trojan

Institute of Chemical Technology, Lenin Sqr. 565, Pardubice, 532 10 Czechoslovakia

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ABSTRACT

Zinc(II)–calcium(II) cyclotetraphosphates have been synthesized as new binary compounds. The synthesis is based on a thermal procedure making use of the reversible transformation of cyclotetraphosphates to higher linear phosphates. With respect to the proposed application of these products as special inorganic pigments the following properties have been determined: density, thermal stability and anticorrosion activity.

1 INTRODUCTION

The cyclotetraphosphates of some divalent metals have been prepared by the authors and examined for potential applications as special inorganic pigments.[1] It appears economically advantageous to replace a part of the cation (divalent metal) by some cheaper divalent element which could also improve, in some cases, special pigment properties. Such an element, in itself, however, does not give the cyclotetraphosphate.[2,3] Reviews which, *inter alia*, mention a number of binary compounds of the type of condensed phosphates made no reference[2–5] to binary zinc–calcium tetraphosphates, the synthesis and properties of which are now reported by us.

2 EXPERIMENTAL PROCEDURE

2.1 General

The procedure for preparation of the binary zinc–calcium cyclotetraphosphates[6] is based on a two-step thermal synthesis. The first step, starting from

Dyes and Pigments 0143-7208/90/$03·50

the pure cyclotetraphosphates of the two divalent metals, involves their melting in a normal air atmosphere and then abruptly cooling to give a vitreous amorphous product composed of higher linear phosphates of the summary formula $(Zn_{2-x}Ca_x)_{n/4}H_2P_nO_{3n+1}$.[7] In the second step this product is repeatedly heated to a suitable temperature and recrystallized to give the microcrystalline product $Zn_{2-x}Ca_xP_4O_{12}$.

2.2 Preparation of $Zn_2P_4O_{12}$ and $Ca(PO_3)_2$

The starting phosphates were prepared on the basis of the previously described thermal method.[2] This procedure was modified by us[8] to obtain the phosphates as pure as possible.[1]

$$\begin{aligned} M^{II}CO_3 + 2H_3PO_4 \xrightarrow[-H_2O,\,-CO_2]{170(200)^\circ C} M(H_2PO_4)_2 \xrightarrow[-H_2O]{260(240)^\circ C} \\ MH_2P_2O_7 \xrightarrow[400^\circ C]{\overset{325^\circ C}{\xrightarrow{-H_2O}}} \begin{matrix} Zn_2P_4O_{12} \\ Ca(PO_3)_2 \end{matrix} \\ M^{II} = Zn(Ca),\ pH_2O_{(g)} \rightarrow 100\,kPa \end{aligned} \tag{1}$$

2.3 Preparation of $Zn_{2-x}Ca_xP_4O_{12}$

The synthesis is outlined in the scheme of reactions (2).

$$\begin{aligned} \left(1-\frac{x}{2}\right)Zn_2P_4O_{12} + xCa(PO_3)_2 + \frac{4}{n}H_2O \xrightarrow[\text{(wet-air-atmosphere)}]{960^\circ C} \\ \frac{4}{n}(Zn_{2-x}Ca_x)_{n/4}H_2P_nO_{3n+1(l)} \xrightarrow[\text{solid}]{960 \rightarrow 25^\circ C} \\ \frac{4}{n}(Zn_{2-x}Ca_x)_{n/4}H_2P_nO_{3n+1(glass)} \xrightarrow{T_{recryst.}} Zn_{2-x}Ca_xP_4O_{12(cryst)} + \frac{4}{n}H_2O \end{aligned} \tag{2}$$

Values of x are 0·25, 0·50, 0·75, 1·00, 1·05 and 1·10. In addition, the same two-step procedure was also applied to the pure $Zn_2P_4O_{12}$ ($x = 0$) and pure $Ca(PO_3)_2$. The mixtures were melted on platinum dishes in an electric furnace by heating to 960°C, i.e. above the melting temperature of the higher-melting starting phosphate [$Ca(PO_3)_2$: 920°C]. After 30 min, the melts were removed from the furnace and abruptly cooled by immersion in water. The resultant vitreous products, $(Zn_{2-x}Ca_x)_{n/4}H_2P_nO_{3n+1}$, were dried at 105°C and ground in a vibrating pebble mill. The intermediates were then calcinated at $T_{max} + 20$°C for 30 min. The sintered blocks of the final products thus obtained were ground in a vibrating pebble mill and the yields (α) were determined by an analytical extraction method.[9]

2.4 Evaluation of quality of the starting phosphates, intermediates and products

The evaluations were carried out using chromatography,[10] IR spectroscopy,[11] X-ray diffraction analysis[12] and atomic absorption spectroscopy.

2.5 Determination of structural parameters of $Zn_{2-x}Ca_xP_4O_{12}$

The products were studied by means of X-ray powder diffraction [$\lambda Cu_{K\alpha} = 0{\cdot}154\,18$ (Ref. 13)]. The diffractograms were indexed under the presumption that the binary cyclotetraphosphates are isostructural with $Zn_2P_4O_{12}$;[11] the lattice parameters of the monoclinic elementary cell (*C*2*c* group) were calculated by the least squares treatment.

2.6 Estimation of properties of products

The products were also evaluated by pycnometry to estimate their density and by the DTA method[14] and by high-temperature microscopy to estimate their temperatures of melting.

The products were also evaluated with respect to the proposed application as new anticorrosion pigments.[15] First, the authors compared the corrosion of steel sheets immersed in the pigment extracts for 8 days. These extracts were prepared by extracting 10 g of pigment with 90 ml of distilled water for 24 h; 2 h of which were with stirring.[16] Next, the pH changes of the pigment extracts on the contact with steel sheets were examined.[16] Finally, the authors prepared and evaluated the oil coating compositions containing the products. The compositions were prepared in a dispergator type Attritor-De 034S (Stephan Werke, BRD) from the following components: 29% linseed oil, 9·2% $Zn_{2-x}Ca_xP_4O_{12}$, 54% Fe_2O_3 (Bayferox 130), 6·6% talc, 1·2% siccative (1% solution of cobalt(II) octanoate in petroleum spirit). These coating compositions were applied to steel sheets and submitted to laboratory tests of prospective efficiency (Table 4, 5, Fig. 5):

—corrosion test with vapours of 18% hydrochloric acid for 8 days;[17]
—corrosion test with condensation of water vapour;[18]
—accelerating test of point coatings resistance against undercorrosion (the method used by Machu and Schiffman).[19]

3 RESULTS AND DISCUSSION

Figure 1 represents the DTA curves of the vitreous intermediates, $(Zn_{2-x}Ca_x)_{n/4}H_2P_nO_{3n+1}$. The first sections indicate an exothermic process.

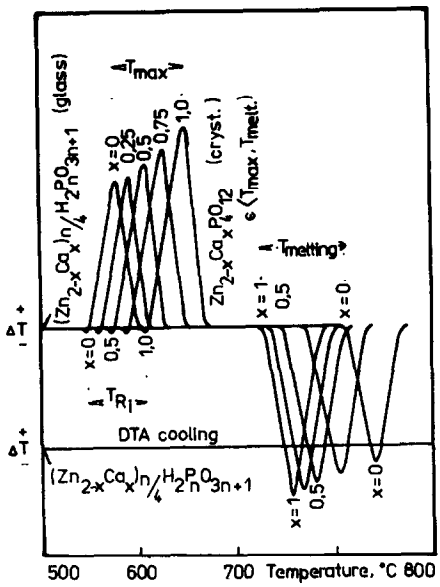

Fig. 1. DTA curves indicating the formation (2) of $Zn_{2-x}Ca_xP_4O_{12}$ and their melting characteristics (3). Apparatus, DTA 1700/DSC Mode Perkin Elmer; sample weight, 15 mg; T increase, 20°C min^{-1}; platinum-crucible open; atmosphere, air.

This process represents the reaction of formation of the cyclotetraphosphate which is related to the initial softening and subsequent recrystallization [reaction (2)] of the amorphous vitreous phase.[6,7] The temperatures (T_{Ri}, T_{max}) and heats (ΔH) of this process, determined from the results of the DTA, increase with increasing calcium content (Table 1; Fig. 2).

The yields (α) of the synthesis are high and also increase with increasing calcium content; the molar ratio P_2O_5 (Zn + Ca) in the extracted 0·3M-HCl products varies from 0·9974 to 1·0025, and the molar ratio Zn/Ca corresponds to the values $(2-x)/x$. Each product represents only a single phase, and its anion corresponds to cyclotetraphosphate. Hence, the products are of the type binary Zn(II)–Ca(II) cyclotetraphosphates of formula $Zn_{2-x}Ca_xP_4O_{12}$. However, X-ray diffraction analysis showed that

TABLE 1
The Conditions of Formation of $Zn_{2-x}Ca_xP_4O_{12}$

	$x=0$	$x=0{\cdot}25$	$x=0{\cdot}5$	$x=0{\cdot}75$	$x=1{\cdot}0$
T_{Ri} (°C)	545	558	573	590	610
T_{max} (°C)	573	586	602	620	630
$-\Delta H$ ($J\,g^{-1}$)	149	155	163	172	182
Yield, α (%)	90·5	93·2	94·8	95·6	96·0

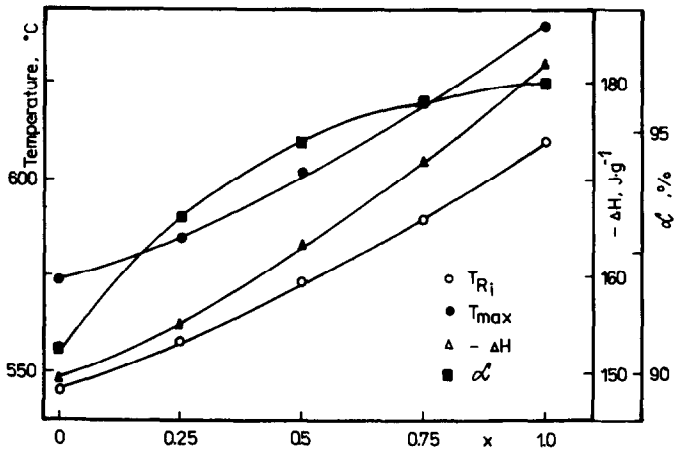

Fig. 2. Values showing the reaction of formation of $Zn_{2-x}Ca_xP_4O_{12}$ and its dependence on the calcium content (x). T_{Ri}, the temperature at the beginning of the reaction (○); T_{max}, the temperature of the maximum exothermic effect (Fig. 1) (●); $-\Delta H$, the heat of the process (▲); α, the yield of the process (■).

no binary products[10] are formed within the whole range of x (Table 2; Fig. 3).

It is apparent that the volume of the primitive unit cell of the binary cyclotetraphosphate increases with the Ca(II) content, which agrees with the fact that its radius is greater than that of Zn(II). At a molar ratio of Zn/Ca = 1 in the product, there appears a break in the dependence of the primitive unit cell volume and lattice parameters on the Ca(II) content. At higher Ca(II) proportions in the product, the values of these are practically constant. The diffractograms then exhibit lines of a further phase. This indicates that it is possible to prepare binary Zn(II)–Ca(II) cyclotetraphosphates with a molar ratio of Ca/Zn ≤ 1.[20] Hence, the existence of this type of

TABLE 2
The Structural Parameters of $Zn_{2-x}Ca_xP_4O_{12}$

x	a (*nm*)	b (*nm*)	c (*nm*)	β (°C)	V (nm^3)	Δ^a
0	1·177 8(5)	0·830 5(4)	0·991 0(4)	118·83(3)	0·849 2	0·011
0·25	1·189 3(4)	0·833 9(3)	0·996 7(5)	118·71(2)	0·866 2	0·010
0·50	1·198 7(5)	0·837 6(6)	1·002 5(5)	118·59(3)	0·883 4	0·012
0·75	1·209 1(3)	0·841 2(3)	1·008 3(4)	118·47(2)	0·900 7	0·009
1·00	1·219 5(6)	0·844 8(7)	1·014 8(6)	118·36(4)	0·920 0	0·014
1·05	1·218 6(10)	0·847 9(7)	1·013 9(6)	118·17(9)	0·922 7	0·013
1·10	1·218 3(9)	0·847 5(7)	1·013 7(8)	118·16(9)	0·922 9	0·014

$^a\Delta = 1/N\sum_1^N|2\theta_{exp} - 2\theta_{calc}|$, where $2\theta_{exp}$ is the experimental diffraction angle, $2\theta_{calc}$ is the angle calculated from lattice parameters and N is the number of diffraction lines investigated.

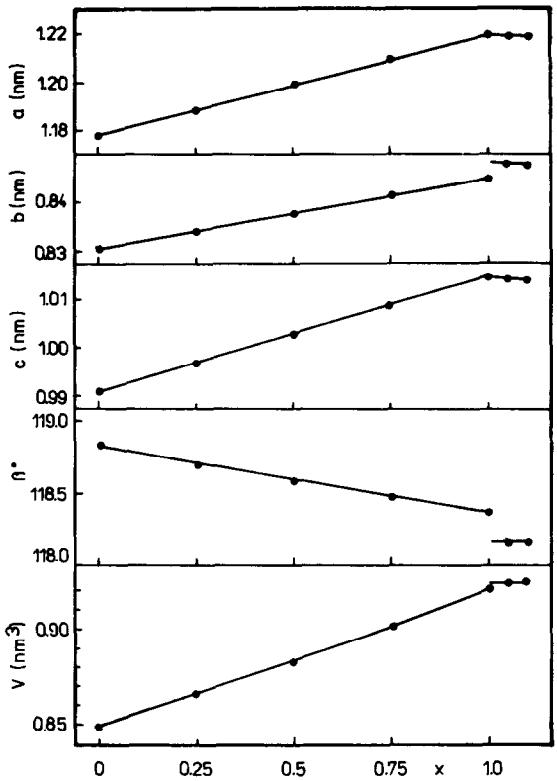

Fig. 3. Structural parameters a, b, c and β and the volume V of the primitive unit cell of $Zn_{2-x}Ca_xP_4O_{12}$.

product containing a higher calcium content than that corresponding to the ratio given cannot be expected.

Some physical properties of the products determined with respect to their potential application as pigments are summarized in Table 3 (Fig. 4); the products are white.

The endothermic effects in the DTA curves (Fig. 1) indicate that (as is confirmed by high-temperature microscopy) their melting in the normal air atmosphere shows variable characteristics [reaction (3)], the cyclotetra-

TABLE 3
Melting Temperatures and Densities of $Zn_{2-x}Ca_xP_4O_{12}$

	$x = 0$	$x = 0{\cdot}25$	$x = 0{\cdot}50$	$x = 0{\cdot}75$	$x = 1{\cdot}00$
$T_{melting}$ (°C)	810	770	748	735	730
ρ_{exp} (g cm^{-3})	3·50	3·42	3·30	3·19	3·05
ρ_{calc} (g cm^{-3})	3·493	3·380	3·267	3·155	3·042

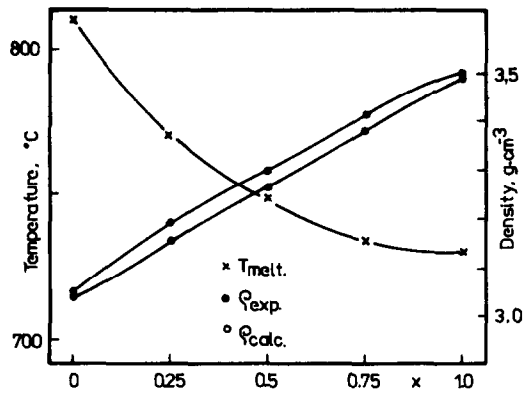

Fig. 4. Dependence of melting temperatures (×) and experimental (●) and calculated densities (○) of the products $Zn_{2-x}Ca_xP_4O_{12}$ on the calcium content (x).

phosphates being transformed into higher linear phosphates,[7] a process which is favoured by the presence of at least traces of water vapour in the air atmosphere.[7]

$$\frac{n}{4}Zn_{2-x}Ca_xP_4O_{12(cryst)} + H_2O = (Zn_{2-x}Ca_x)_{n/4}H_2P_nO_{3n+1(l)} \qquad (3)$$

The density of the products changes with the calcium content, the values decreasing with increasing x (ρ_{exp} being in accord with the ρ_{calc} values, Fig. 4).

Tests on the protective efficiency demonstrate the efficiency of the binary

TABLE 4
Evaluation of the Inhibition Ability of Powdery $Zn_{2-x}Ca_xP_4O_{12}$

Pigment	*pH of aqueous extract of powdery product*			*Mass decrease of the steel due to corrosion during 8 days immersion in the aqueous extract of pigment* ($mg\,g^{-1}$)
	Original	*Eight days after immersion of steel sheet into the extract*	*Eight days after removal of steel sheet from the extract*	
$Zn_2P_4O_{12}$	5·40	6·19	5·58	1·072
$Zn_{1.75}Ca_{0.25}P_4O_{12}$	5·69	6·44	5·90	0·825
$Zn_{1.5}Ca_{0.5}P_4O_{12}$	5·98	6·65	6·26	0·654
$Zn_{1.25}Ca_{0.75}P_4O_{12}$	6·25	6·73	6·42	0·570
$ZnCaP_4O_{12}$	6·40	6·82	6·49	0·631
$Ca(PO_3)_2$	6·42	6·98	6·62	1·033

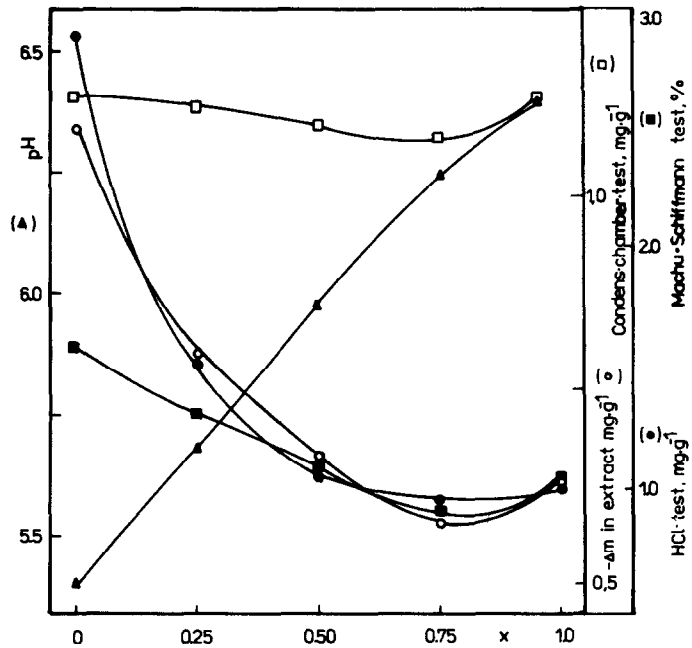

Fig. 5. Dependence of values obtained from anticorrosion tests with $Zn_{2-x}Ca_xP_4O_{12}$ on calcium content (see Tables 4 and 5). △, pH of extract (original); ○, loss in steel weight due to corrosion in the extract; ●, test in HCl vapour; □, test in condensation chamber; ■, Machu & Schiffman test.[19]

Zn–Ca cyclotetraphosphates in anticorrosion-inhibition (Tables 4 and 5). Most values are distinctly better than those obtained with reference samples containing a commercial anticorrosion pigment of the type of a simple Zn(II) phosphate dihydrate ($Zn_3(PO_4)_2 . 2H_2O$).[16] This effect is due to the higher content of the phosphoric component in cyclotetraphosphates and also by the fact that the passive simple phosphate ions can be released gradually from these slightly soluble compounds, the release being controlled practically by the extent of the corrosion action of the humid medium (after gradual splitting of the cyclic tetraphosphate anion).[21]

The anticorrosion-inhibition action of Zn(II) ions represents an additional favourable factor. The additional presence of Ca(II) ion causes an alkalinity increase (i.e. acidity lowering) of the binary products (see the pH values in Table 4), which again favourably affects the anticorrosion-inhibition ability. Therefore, the binary Zn(II)–Ca(II) cyclotetraphosphates prove to be more efficient than the pure Zn(II) cyclotetraphosphate (Fig. 5) and the corresponding calcium derivative. It is also apparent that there exists an optimum with respect to the calcium content in the binary products $Zn_{2-x}Ca_xP_4O_{12}$ with $x \in (0; 1)$; this optimum lies near $x = 0{\cdot}75$ (see the minima on the curves in Fig. 5).

TABLE 5
Evaluation of Anticorrosion Properties of Oil Coating Composition Containing 9·2% (w/w) $Zn_{2-x}Ca_xP_4O_{12}$

Pigment	*Steel weight decrease due to corrosion with application of the pigment-containing coating* ($mg\,g^{-1}$)		*Area of damaged coating (near a cut 100 mm long) in a rapid immersion test of resistance against undercorrosion (according to Machu & Schiffman)*	
	After 28 days in condensation chamber	*After 8 days in HCl vapours*	(mm^2)	(%)
$Zn_2P_4O_{12}$	1·13	2·885	15·0	1·67
$Zn_{1·75}Ca_{0·25}P_4O_{12}$	1·11	1·501	11·7	1·30
$Zn_{1·5}Ca_{0·5}P_4O_{12}$	1·10	1·022	9·7	1·07
$Zn_{1·25}Ca_{0·75}P_4O_{12}$	1·08	0·961	8·0	0·89
$ZnCaP_4O_{12}$	1·12	0·983	9·3	1·03
$Ca(PO_3)_2$	1·40	1·290	11·0	1·22

4 CONCLUSION

We have shown that it is possible to prepare binary Zn(II)–Ca(II) cyclotetraphosphates, $Zn_{2-x}Ca_xP_4O_{12}$, where $x \in (0; 1\rangle$. (However, the existence of this type of product with the Ca/Zn molar ratio above 1 cannot be expected.) The colourless (white) products crystallize in the monoclinic system, in the $C2c$ group. Their structural parameters have the values: $a = 1·1778$–$1·2195$ nm, $b = 0·8305$–$0·8448$ nm, $c = 0·9910$–$1·0148$ nm, $\beta = 118·30$–$118·83°$ (the volume of the primitive unit cell increases from $0·8492\,nm^3$ to $0·9200\,nm^3$ with increasing proportion of calcium in the product). Melting temperatures and densities decrease with increasing calcium content (the respective intervals are 810–730°C and 3·50–3·05 $g\,cm^{-3}$).

The binary Zn(II)–Ca(II) cyclotetraphosphates $Zn_{2-x}Ca_xP_4O_{12}$ exhibit very good anticorrosion-inhibition properties; their maximum value is obviously reached at a Zn/Ca molar ratio in the region of 1·67.

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