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Binary cyclo-tetraphosphates ($Co_{2-x}Ca_xP_4O_{12}$) as special pigments

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The cyclo-tetraphosphates of the type $Co_{2-x}Ca_xP_4O_{12}$, where $x = 0$ to 1, have been synthesized as new binary compounds, and their existence has been proved. The synthesis is based on a thermal procedure making use of the reversible transformation of cyclo-tetraphosphates to higher linear phosphates. Temperatures and heats of formation of these products have been determined (i.e. formation by thermal recrystallization from higher linear phosphates) along with the yields of this procedure which increase with increasing x (the calcium content). The structure of the binary cyclo-tetraphosphates belongs to the monoclinic system (over the whole range of x); the structural parameters determined usually increase with increasing calcium content. With respect to the proposed application of these products as special inorganic pigments, the following properties have been determined experimentally: density, thermal stability, colour hue and the anticorrosion activity.

1. Introduction

The cyclo-tetraphosphates of some divalent metals, including $Co_2P_4O_{12}$, have been prepared in our laboratory and examined for potential applications as special inorganic pigments [1, 2]. The purposes involved comprise high-temperature applications (e.g. in ceramics [3, 4], anticorrosion purposes [5, 6], and luminescence [7, 8]). It appears economically advantageous to replace part of the cobalt by some cheaper divalent element which, in addition, could also improve, in some cases, the special pigment properties. Such a suitable element, in our opinion, is calcium, which in itself, does not give the cyclo-tetraphosphate [9]. Therefore, the binary cobalt–calcium tetraphosphates with cyclic anions have not been described in literature to date. Even the newest reviews [10–12], which also mention a number of binary compounds of the type of condensed phosphates, refuse to accept their existence.

Therefore, we examined the possibility of the thermal preparation of binary Co(II) and Ca(II) cyclo-tetraphosphates by a procedure developed in our laboratory for other purposes [13]. The anhydrous products were prepared by calcination of the starting mixtures of Co(II) and Ca(II) carbonates and phosphoric acid (the molar ratio $Me(II)/P_2O_5 = 1$) under conditions of enhanced water vapour pressure [14, 15]. These products were then heated above the melting temperature of $Co_2P_4O_{12}$ and by remelting, were transformed into higher polyphosphates. Their abrupt cooling gave homogeneous phosphate glasses of the formula $(Co_{2-x}Ca_x)_{n/4}H_2P_nO_{3n+1}$ which were then reheated to a relatively narrow temperature interval to be recrystallized into a compound of cyclo-tetraphosphate type.

The revelation of the existence of the new compounds – the binary cobalt(II)–calcium(II) cyclo-tetraphosphates – as well as the method of their thermal preparation documented in the present paper are dealt with in Czechoslovak patents [16, 17]; a similar situation is also encountered with the synthesis of the products mentioned at lower temperatures [18] and their applications as thermostable coloured anti-corrosion pigments [19].

2. Experimental details

2.1. Preparation of the pure starting phosphates $Co_2P_4O_{12}$ and $Ca(PO_3)_2$

The starting phosphates were prepared on the basis of the thermal method described previously [9]. In our laboratory this procedure was modified in order to obtain the phosphates as pure as possible [14, 15]. This result was achieved first of all by the use of increased water vapour pressure in the calcination area and by precise determination of the temperatures of the individual Reactions 1 to 4 by the methods of thermal analysis under quasi-isobaric and quasi-isothermal conditions [20, 21] (Table I).

$$M^{II}CO_3 + 2H_3PO_4 \overset{T_1}{\rightleftharpoons} M(H_2PO_4)_2 + H_2O + CO_2 (M^{II} = \text{Co or Ca}) \quad (1)$$

$$M(H_2PO_4)_2 \overset{T_2}{\rightleftharpoons} MH_2P_2O_7 + H_2O \quad (2)$$

$$2CoH_2P_2O_7 \overset{T_3}{\rightleftharpoons} Co_2P_4O_{12} + 2H_2O \quad (3)$$

$$CaH_2P_2O_7 \overset{T_4}{\rightleftharpoons} Ca(PO_3)_2 + H_2O \quad (4)$$

The applied carbonates of the individual metals and phosphoric acid were of p.a. purity grade (the acid concentration was 40% by wt H_3PO_4); their mixtures corresponding to the left-hand side of Equation 1 were

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TABLE I The temperatures (°C) of the individual reactions in the synthesis of $Co_2P_4O_{12}$ and $Ca(PO_3)_2$ ($pH_2O_{(g)}$ = 100 kPa)

	T_1	T_2	T_3	T_4
$Co_2P_4O_{12}$	105-*180*	180-*240*	280-*295*	-
$Ca(PO_3)_2$	170-*200*	200-*240*	-	*400*

calcinated separately in an electric muffle furnace (L 112.2 VEB Frankenhausen, East Germany). The rate of temperature increase was 2°C min^{-1}, the temperatures T_1 to T_4 being maintained 60 min each. The final calcination was always done at 600° C for 3 h. The carrier of the calcinated mixture consisted of six platinum crucibles in a labyrinth arrangement, which ensured a water vapour pressure of about 100 kPa in the calcination area. Thereafter the cyclo-tetraphosphates were purified by extraction with 0.3 M HCl to remove all the side products [21]. The quality of the product was confirmed by instrumental analytical methods.

2.2. Preparation of $Co_{2-x}Ca_xP_4O_{12}$

The following scheme describes our procedure for the synthesis of $Co_{2-x}Ca_xP_4O_{12}$ [5]

$$\begin{aligned}
&(1 - x/2)Co_2P_4O_{12} + xCa(PO_3)_2 + 4/nH_2O \\
&\xrightarrow[\text{(air-wet-atmosphere)}]{\text{melting (920 to 1060° C)}} 4/n\,(Co_{2-x}Ca_x)_{n/4}H_2P_nO_{3n+1(l)} \\
&\xrightarrow[\text{solidification}]{\text{1060 to 25° C}} 4/n(Co_{2-x}Ca_x)_{n/4}H_2P_nO_{3n+1\,(glass)} \\
&\xrightarrow{T\text{ recrystallization}} Co_{2-x}Ca_xP_4O_{12}(\text{cryst.}) + 4/nH_2O
\end{aligned} \tag{5}$$

The mixtures for synthesis of the binary products were prepared from the simple starting cyclo-tetraphosphates whose ratio was adjusted to make the x value equal to 0.25, 0.5, 0.75, 1.0, 1.05 and 1.1. In addition, the same two-step procedure was also applied to the pure $Co_2P_4O_{12}$ (x = 0) and pure $Ca(PO_3)_2$. The mixtures were homogenized in an agate mortar and then melted on platinum dishes in the electric furnace L 112.2 by heating to 1100° C, i.e. above the melting temperature of the higher-melting starting phosphate ($Co_2P_4O_{12}$: 1060° C). After 30 min, the dishes with melts were removed from the furnace and abruptly cooled by immersion in water. The vitreous products obtained of the higher linear phosphates type, $(Co_{2-x}Ca_x)_{n/4}H_2P_nO_{3n+1}$, were dried at 115° C and ground in a vibrating pebble mill. Other aliquots of these intermediates were then subject to differential thermal analysis (DTA) (Fig. 1) in order to find the temperatures of the exothermic processes of thermal recrystallization. These temperatures correspond to those of the formation of the binary cobalt–calcium cyclo-tetraphosphates (Table II, Fig. 2); therefore, the individual intermediates were then calcined in the electric furnace L 112.2 at temperatures higher by 20° C (T_{max} + 20° C) for 30 min. The sintered blocks of the individual final products obtained in this way were ground in the vibrating pebble mill, weighed (mass m_1), and extracted with a hundred-fold amount of 0.3 M HCl for 2 h; the solid was separated by filtration, dried at 115° C, and weighed (m_2).

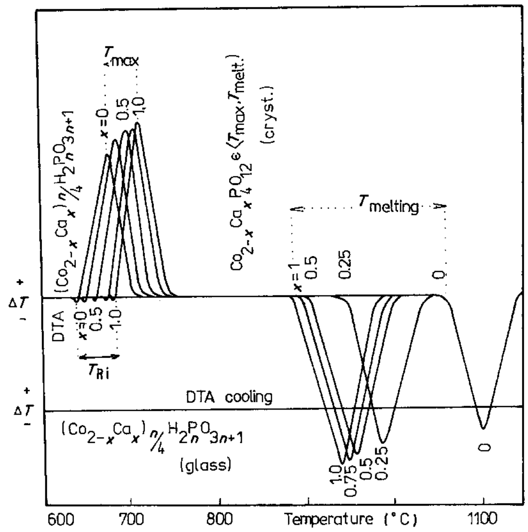

Figure 1 The DTA curves of the vitreous intermediates $(Co_{2-x}Ca_x)_{n/4}H_2P_nO_{3n+1}$ indicating the formation of the products $Co_{2-x}Ca_xP_4O_{12}$ (by Reaction 6) and their incongruent melting (7); sample weight 15 mg, temperature increase 20°C min^{-1}, open platinum crucible, air atmosphere.

TABLE II The conditions of formation of $Co_{2-x}Ca_xP_4O_{12}$

	x				
	0	0.25	0.5	0.75	1.0
T_{Ri}(° C)	635	644	656	667	674
T_{max}(° C)	673	682	690	696	702
$-\Delta H$(J g^{-1})	130	139	150	163	179
yields, α(%)	98.20	98.05	97.70	97.52	97.40

2.3. The applied methods of instrumental analysis

2.3.1. Evaluation of the quality of the starting phosphates, intermediates, and products

The evaluation was carried out by chromatography [22, 23] with a TLC II set (Kavalier Sázava ČSSR), infrared spectroscopy [24] with a Perkin Elmer 684 Infrared Spectrophotometer, X-ray diffraction analysis [25, 26] with a HZG-4 (East Germany). The extraction method developed in our laboratory (with 0.3 M HCl) [27] was also used: vitreous intermediates

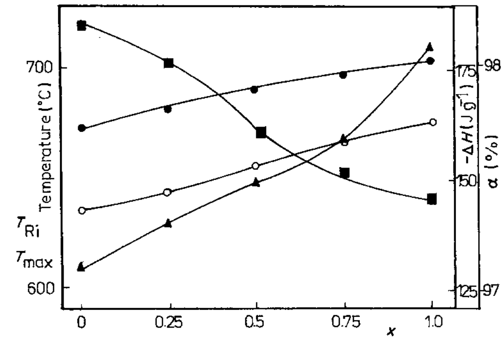

Figure 2 The values documenting Reaction 6 of the formation of $Co_{2-x}Ca_xP_4O_{12}$ for the dependence on the calcium content (x); T_{Ri}, the temperatures of the beginning of the reaction (○); T_{max}, the temperatures of the maxima of exothermic effects (Fig. 1) (●); $-\Delta H$, the heats of the process (▲); α, the yields of the process (■).

TABLE III The structural parameters of $Co_{2-x}Ca_xP_4O_{12}$

x	a(nm)	b(nm)	c(nm)	β(deg)	V(nm^3)	Δ*	Number of phases	
0	1.1799(5)	0.8304(7)	0.9887(7)	118.70(3)	0.8497	0.013	one	$Co_{2-x}Ca_xP_4O_{12}$
0.25	1.1878(12)	0.8391(9)	0.9895(9)	118.73(6)	0.8663	0.017	one	$Co_{2-x}Ca_xP_4O_{12}$
0.50	1.1932(8)	0.8439(6)	0.9901(6)	118.75(4)	0.8741	0.012	one	$Co_{2-x}Ca_xP_4O_{12}$
0.75	1.1968(13)	0.8546(9)	0.9878(10)	118.79(6)	0.8853	0.018	one	$Co_{2-x}Ca_xP_4O_{12}$
1.00	1.2130(7)	0.8676(5)	0.9874(6)	118.90(3)	0.9135	0.009	one	$Co_{2-x}Ca_xP_4O_{12}$
1.05	1.2138(9)	0.8678(7)	0.9885(7)	118.69(5)	0.9153	0.003	more than one	mixtures
1.10	1.2147(6)	0.8676(5)	0.9895(5)	118.47(3)	0.9165	0.008		mixtures

*$\Delta = 1/N\Sigma_1^N \, |2\theta_{exp} - 2\theta_{calc}|$, 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 investigated diffraction lines.

of the type of higher linear phosphates are dissolved, whereas cyclo-tetraphosphates resist the extraction. Hence, in the cases when binary cyclo-tetraphosphates are formed without any further crystalline phase (see below) it is possible to determine the yield of recrystallization from the relation m_2/m_1 (Section 2.2., Table II, Fig. 2). The sample aliquots of the individual products were dissolved by boiling in 15% HCl (several days) and analysed by means of atomic absorption spectrometry [28] to determine the ratios $P_2O_5/(Co + Ca)$ and Co/Ca.

2.3.2. Determination of the structural parameters of $Co_{2-x}Ca_xP_4O_{12}$

X-ray diffractograms of the samples were obtained using a vertical X-ray diffractometer HZG-4B (VEB Freiberger Präzisionsmechanik, East Germany), equipped with a goniometer of 25 cm diameter and a proportional detector. Cu$K\alpha$ radiation was used with the elimination of $K\beta$ radiation by a nickel filter; in the range $2\theta = 10°$ to $35°$ the interplanar spacing was calculated using Cu$K\alpha$ radiation ($\lambda = 0.154\,178$ nm) and in the range $2\theta = 35°$ to $90°$, Cu$K\alpha_1$ radiation ($\lambda = 0.154\,051$ nm) was used.

Powdered silicon (a = 543 055 nm) served as an external standard. The lattice parameters were computed using the least squares technique to increase the accuracy, the minimized quantity being $(2\theta_{exp} - 2\theta_{calc})^2$. The diffractograms were indexed on the basis of the binary cobalt(II)-calcium(II) cyclo-tetraphosphates being isostructural with $Co_2P_4O_{12}$ which crystallize in the monoclinic system, C/2c group [25, 26]. The least squares treatment was adopted to calculate the lattice parameters of the elementary monoclinic cell of the binary products (Table III); their dependences on the amount of calcium in the products are presented in Fig. 3.

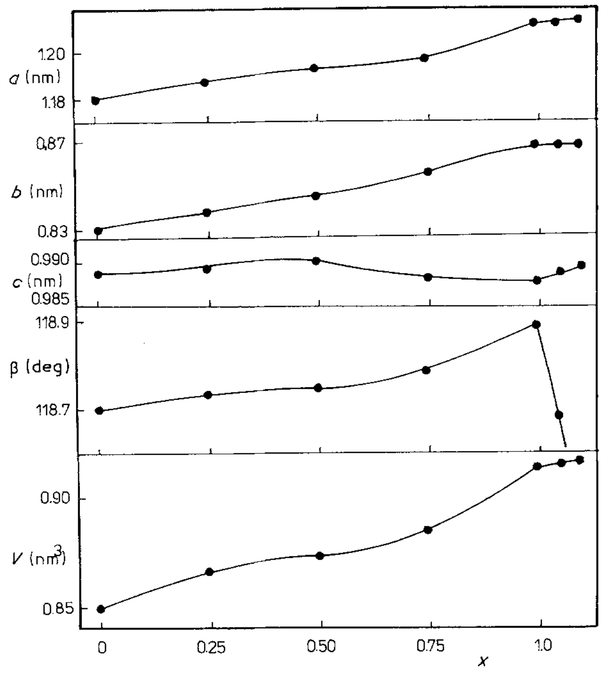

Figure 3 The structural parameters a, b, c and β and the volume, V, of the elementary unit cell of $Co_{2-x}Ca_xP_4O_{12}$.

2.3.3. Estimation of some physical properties

The products were analysed by the pycnometric method [29] to estimate their density and by the DTA method (DTA-1700 with DSC Mode, Perkin Elmer) [30] along with high-temperature microscopy MHO-2, Zeiss, Jena) to estimate their temperatures and heats of formation (the values found are given in Table IV, and their dependence on the amount of calcium in the products is presented in Fig. 4).

The reflectance factor of the products in the visible light region was measured using a Specol 10 apparatus (Zeiss, Jena) equipped with the respective 45/0 adaptor (Fig. 5). Because of the proposed application as new anticorrosion pigments [19], the products were also evaluated from this point of view. First we compared the corrosion of steel sheets immersed in the pigment

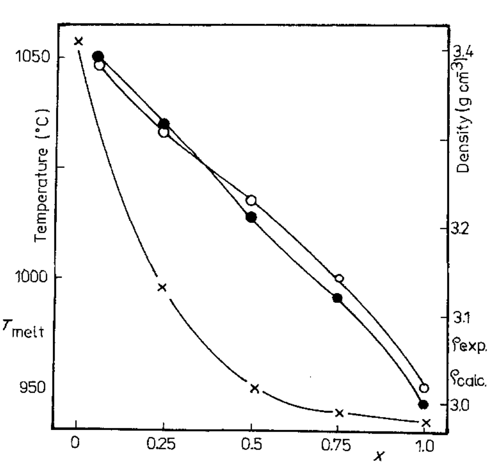

Figure 4 The dependence of (x) melting temperatures and (●) experimental and (○) calculated densities of the products $Co_{2-x}Ca_xP_4O_{12}$ on the calcium content (x).

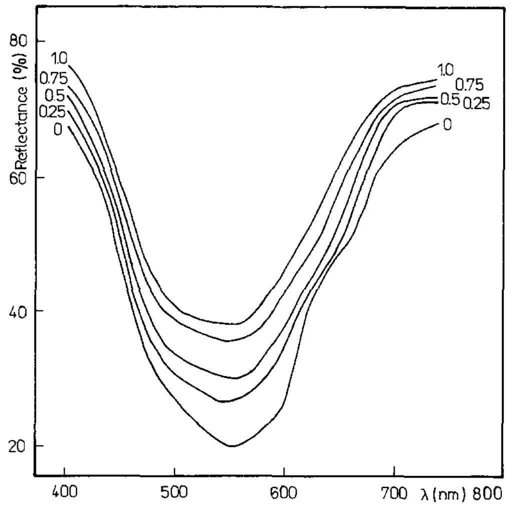

Figure 5 The reflectance curves (colour) of $Co_{2-x}Ca_xP_4O_{12}$.

extracts for 8 days (the extracts were prepared by extracting 10 g pigment with 90 ml distilled water for 24 h with 2 h stirring [31]). Next we examined the pH changes of the pigment extracts on contact with the steel sheets [31]. Finally, we also prepared and evaluated oil coating compositions containing our products. The compositions were prepared an a dispergator type Attritor-De 034S (Stephan Werke, West Germany) from the following components: 29% linseed oil, 9.2% $Co_{2-x}Ca_xP_4O_{12}$, 54% Fe_2O_3 (Bayferox 130), 6.6% talc, 1.2% dehydrator (1% solution of cobalt (II) octanoate in petroleum spirit). These coating compositions were applied to steel sheets which were then submitted to the following laboratory tests of protective efficiency (Tables V and VI, Fig. 6):

(i) corrosion test with 18% hydrochloric acid vapours for 8 days [32],

(ii) corrosion test with condensation of water vapour [33],

(iii) accelerating test of point coating resistance against undercorrosion by Machu and Schiffman's method [34].

3. Results and discussion

Fig. 1 shows the DTA curves of the vitreous intermediates $(Co_{2-x}Ca_x)_{n/4}H_2P_nO_{3n+1}$ for $x = 0, 0.25, 0.5, 0.75, 1.0$, and 2.0. Their first sections (up to 700° C) indicate an exothermic process. This process represents the formation reaction of the cyclo-tetraphosphate which is connected with initial softening and subsequent recrystallization of the amorphous vitreous phase [6].

$$(Co_{2-x}Ca_x)_{n/4}H_2P_nO_{3n+1(\text{glass})} = n/4\ Co_{2-x}Ca_xP_4O_{12(\text{cryst})} + H_2O_{(g)} \quad (6)$$

TABLE IV Melting temperatures and densities of $Co_{2-x}Ca_xP_4O_{12}$

	x				
	0	0.25	0.50	0.75	1.0
T_{melting}(° C)	1060	945	900	890	885
ϱ_{exp}(g cm^{-3})	3.40	3.32	3.21	3.12	3.00
ϱ_{calc}(g cm^{-3})	3.391	3.290	3.224	3.148	3.017

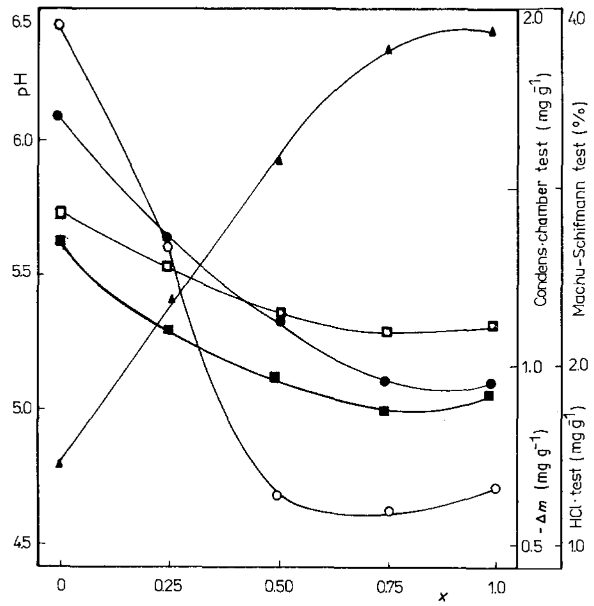

Figure 6 Dependence of values obtained from anticorrosion tests with $Co_{2-x}Ca_xP_4O_{12}$ on calcium content (see Tables V and VI). (▲) pH of extract (original), (○) loss in steel weight due to corrosion in the extract, (●) test in HCl vapour, (□) test in condensation chamber, (■) test by Machu and Schiffman [34].

Both the temperatures and heats of this process determined under the conditions of thermal analysis (Table II, Fig. 2) indicate that increasing the calcium content is connected with a continuous increase of both the temperature of the beginning and the temperature of the maximum of the exothermic effects and the heat of the process.

The analysis of the products prepared on a larger scale in electric furnaces at temperatures $T_{\max} + 20°$ C showed that the yields of this synthesis are high (decrease with increasing calcium content). The molar ratio $P_2O_5/(Co + Ca)$ determined in the extracted products varies from 0.9995 to 1.0004, and the mutual ratio of the divalent metals, Co/Ca, corresponds very precisely to the values $(2 - x)/x$. The instrumental analytical methods confirmed that each product represents only a single phase, and composition of its anion corresponds to cyclo-tetraphosphate. From this it follows that the two-step synthesis described succeeded in giving the products of binary cobalt(II)–calcium(II) cyclo-tetraphosphates of the formula $Co_{2-x}Ca_xP_4O_{12}$. However, X-ray diffraction analysis showed that no binary products are formed over the whole range of x (Table III). The dependence of the lattice parameters and volume of the elementary cell on the proportion of the Ca(II) component in the product is given in Fig. 3. It is obvious that the volume of the elementary cell of the binary cyclo-tetraphosphate is increased with the Ca(II) content, which agrees with the fact that its radius is greater than that of Co(II) by about one-fifth. At the molar ratio of Co/Ca = 1 in the product, there appears a break in the dependence of the elementary cell volume and lattice parameters on the Ca(II) content. At higher Ca(II) proportions in the product, the values of the quantities mentioned practically no longer change. The diffractograms then exhibit lines of a further phase. The results thus indicate that it

TABLE V Evaluation of the inhibition ability of powdery $Co_{2-x}Ca_xP_4O_{12}$

Pigment	pH of aqueous extract of powdery product			Mass decrease of the steel due to corrosion during 8 d immersion in the aqueous extract of pigment ($mg\,g^{-1}$)
	original	8 d after immersion of steel sheet into the extract	8 d after removal of steel sheet from the extract	
$Co_2P_4O_{12}$	4.82	5.64	5.02	1.962
$Co_{1.75}Ca_{0.25}P_4O_{12}$	5.42	6.02	5.68	1.354
$Co_{1.5}Ca_{0.5}P_4O_{12}$	5.93	6.45	6.10	0.647
$Co_{1.25}Ca_{0.75}P_4O_{12}$	6.05	6.53	6.22	0.602
$CoCaP_4O_{12}$	6.36	6.89	6.52	0.660
$Ca(PO_3)_2$	6.42	6.98	6.62	1.033

is possible to prepare binary Co(II)–Ca(II) cyclo-tetraphosphates with the molar ratio of $Ca/Co \leqslant 1$. Hence, the existence of this type of product containing a higher calcium content than that corresponding to the ratio given, cannot be expected. (This fact is obviously connected with the non-existence of pure calcium(II) cyclo-tetraphosphate as already stressed in the Section 1.)

Some physical properties of the products determined with respect to their potential application as pigments are summarized in Table IV. As the yields of this synthesis were high, the sections of DTA curves above the recrystallization temperature can be considered to determine the thermal stabilities of the binary cyclo-tetraphosphates. The endothermic effects at these DTA curves document their melting (as confirmed by means of high-temperature microscopy), which is incongruent: the cyclo-tetraphosphates are transformed into higher linear phosphates [7], which is favoured by the presence of at least traces of water vapour in the air atmosphere [35].

$$Co_{2-x}Ca_xP_4O_{12(cryst)} + 4/n\,H_2O_{(g)} = 4/n(Co_{2-x}Ca_x)_{n/4}H_2P_nO_{3n+1(l)} \qquad (7)$$

Hence, under these conditions the melting temperatures represent the temperatures up to which the binary cyclo-tetraphosphates are stable; with the calcium content they decrease from 1060 up to 885° C (Fig. 4). This fact documents high thermostability of the products, which extends the range of their application to high-temperature purposes.

The density of the binary products also continuously changes with the calcium content, however, as expected, in this case the density values decrease with increasing x (which again agrees with the lower density found for $Ca(PO_3)_2$ compared with that found for the pure $Co_2P_4O_{12}$), the experimental values (ϱ_{exp}) being in accordance with the density values calculated (ϱ_{calc}) on the basis of the X-ray diffraction analysis (Fig. 4).

The colour hue of the binary cobalt(II)–calcium(II) cyclo-tetraphosphates is an intense blue–violet; the intensity of the blue-violet hue being decreased with increasing calcium content in the product (Fig. 5).

The results of the laboratory tests of protective efficience showed the effect of the binary Co–Ca cyclo-tetraphosphates in the sense of anticorrosion–inhibition activity (Table V and VI). Most values are distinctly better than those obtained with reference samples containing a commercial anticorrosion pigment of the simple zinc(II) phosphate dihydrate, ($Zn_3(PO_4)_2 \cdot 2H_2O$) type [36]. This result is caused by the higher content of the phosphoric component in cyclo-tetraphosphates and by the fact that the passivating simple phosphate ions can be released gradually from these slightly soluble compounds, the release being practically controlled by the extent of the corrosion action of the humid medium [5, 19] (after gradual splitting of the cyclic tetraphosphate anion [6]). A certain anticorrosion–inhibition action of cobalt(II) ions represents an additional favourable factor [37]. The presence of calcium(II) ions in addition causes an alkalinity increase (or better, acidity decrease) of the binary products (see the pH values in Table V), which again favourably affects the anticorrosion–inhibition ability. Therefore, the binary cobalt(II)–calcium(II) cyclo-tetraphosphates proved to be more efficient than the pure cobalt(II) cyclo-tetraphosphate (Fig. 6) and the corresponding calcium derivative [5]. It is also obvious that there exists a cerain optimum with regard to the calcium content in these binary $Co_{2-x}Ca_xP_4O_{12}$ products with $x = 0$ to 1:

TABLE VI Evaluation of anticorrosion properties of oil coating compositions containing 9.2% (wt/wt) $Co_{2-x}Ca_xP_4O_{12}$

Pigment	Decrease in steel weight due to corrosion with application of the pigment-containing coating		Area of damaged coating (near a cut of 100 mm length) in a rapid immersion test of resistance against undercorrosion (according to Machu and Schiffman [34])	
	after 28 d in condensation chamber ($mg\,g^{-1}$)	after 8 d in HCl vapour ($mg\,g^{-1}$)	(mm^2)	(%)
$Co_2P_4O_{12}$	1.42	3.38	24.3	2.70
$Co_{1.75}Ca_{0.25}P_4O_{12}$	1.28	2.68	19.7	2.18
$Co_{1.5}Ca_{0.5}P_4O_{12}$	1.16	2.28	17.6	1.95
$Co_{1.25}Ca_{0.75}P_4O_{12}$	1.10	1.92	15.8	1.75
$CoCaP_4O_{12}$	1.12	1.93	14.0	1.85
$Ca(PO_3)_2$	1.40	1.29	11.0	1.22

this optimum lies near $x = 0.75$ (see the minima on the curves in Fig. 6).

4. Conclusion

Our work shows that it is possible to prepare binary cobalt(II)–calcium(II) cyclo-tetraphosphates, $Co_{2-x}Ca_xP_4O_{12}$, where $x = 0$ to 1. (However, the existence of this type of product with the Ca/Co mole ratio above 1 cannot be expected.) The products crystallize in the monoclinic system, C/2c group. Their structural parameters have the values: $a = 1.1799$ to 1.2130 nm, $b = 0.8304$ to 0.8676 nm, $c = 0.9877$ to 0.9901 nm, $\beta = 118.70°$ to 118.79° (the volume of the elementary cell increases from 0.8607 to 0.9135 nm^3 with increasing proportion of calcium in the product); the melting temperatures and densities decrease with increasing calcium content (the respective intervals are 1060 to 885° C and 3.0 to 3.4 $g\,cm^{-3}$), the colour hue is an intense blue-violet.

The binary cobalt(II)–calcium(II) cyclo-tetraphosphates, $Co_{2-x}Ca_xP_4O_{12}$, exhibit very good anticorrosion–inhibition properties; their maximum value is obviously reached at the Co/Ca mole ratio in the product near 1.67.

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