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Double Tetrametaphosphates $Mn_{2-x}Ca_xP_4O_{12}$ as Special Pigments

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ABSTRACT

Tetrametaphosphates of type $Mn_{2-x}Ca_xP_4O_{12}$, where $0 \leq x \leq 1$, 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 tetrametaphosphates 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) together with the yields using this procedure, which increase with increasing x (the calcium content). The structure of the binary tetrametaphosphates 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 and anticorrosion activity.

1 INTRODUCTION

The tetrametaphosphates of some divalent metals, $Mn_2P_4O_{12}$ *inter alia*, have been previously prepared by us and examined for potential application as special inorganic pigments.[1,2] The use of such pigments include high-temperature applications (e.g. in ceramics),[3,4] anticorrosion[5,6] purposes and luminescence.[7,8] It appears economically advantageous to replace a part of the manganese by some cheaper divalent element which in some cases, could also improve special pigment properties. Such a suitable element is calcium,

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which itself, however, does not give the tetrametaphosphate[9] and therefore, the binary manganese–calcium tetraphosphates with cyclic anions have not been previously described. Even current reviews[10,11] which *inter alia* mention a number of binary compounds of the condensed phosphate type do not make reference to them.

Therefore we examined the possibility of thermal preparation of double Mn(II) and Ca(II) tetrametaphosphates by the procedure developed in our laboratory for other purposes.[12] The anhydrous products were prepared by calcination of the starting mixtures of Mn(II) and Ca(II) carbonates and phosphoric acid (molar ratio $Me(II)/P_2O_5 = 1$) in conditions of enhanced water vapour pressure.[13,14] The mixtures of these products were then heated above the melting temperature of $Mn_2P_4O_{12}$ and by remelting transformed into higher polyphosphates. Their abrupt cooling gave homogeneous phosphate glasses of formula $(Mn_{2-x}Ca_x)_{n/4}H_2P_nO_{3n+1}$ which were then reheated to a relatively narrow temperature interval to be recrystallized to a compound of tetrametaphosphate type.

The existence of these new compounds, viz. the binary manganese(II)–calcium(II) phosphates, and the method of their thermal preparation as documented in this present communication are dealt with in Czechoslovak patents;[15,16] as are the syntheses of the products mentioned above at lower temperatures[17] and their applications as thermostable anticorrosion pigments.[18]

2 EXPERIMENTAL

2.1 Preparation of the pure phosphate starting materials $Mn_2P_4O_{12}$ and $Ca(PO_3)_2$

The starting phosphates were prepared on the basis of the thermal method described in Ref. 9. In our laboratory this procedure was modified so as to obtain the phosphates as pure as possible. This result was achieved first of all by the use of increased water vapour pressure in the calcination area and by

TABLE 1
The Temperatures (°C) of the Individual Reactions in the Synthesis of $Mn_2P_4O_{12}$ and $Ca(PO_3)_2$ ($pH_2O_{(g)} \sim 100$ kPa)

	T_1	T_2	T_3	T_4
$Mn_2P_4O_{12}$	120	205	310	—
$Ca(PO_3)_2$	170–200	200–240	—	400

precise determination of the temperatures of the individual reactions (1)–(4) by the methods of thermal analysis in quasi-isobaric and quasi-isothermal conditions (Table 1).[19,20]

$$M^{II}CO_3 + 2\,H_3PO_4 \overset{T_1}{=} M^{II}(H_2PO_4)_2 + H_2O + CO_2 \quad (1)$$

$$M^{II}(H_2PO_4)_2 \overset{T_2}{=} M^{II}H_2P_2O_7 + H_2O \quad (2)$$

$$2\,MnH_2P_2O_7 \overset{T_3}{=} Mn_2P_4O_{12} + 2\,H_2O \quad (3)$$

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

$$(M^{II} = Mn, Ca)$$

The individual metal carbonates and phosphoric acid were of p.a. purity grade (the acid concentration was 40% wt H_3PO_4); their mixtures corresponding to the left-hand side of eqn (1) were calcinated separately in an electric muffle furnace (L 112.2, VEB Frankenhausen, GDR). 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 made always at 600°C for 3 h. The carrier of the calcinated mixture consisted of six platinum crucibles in a labyrinth arrangement, which ensured water vapour pressure of about 100 kPa in the calcination area. Thereafter the tetrametaphosphates were purified by extraction with 0·3M-HCl to remove all the side products.[21] The quality of product was confirmed by instrumental analytical methods.

2.2 Preparation of $Mn_{2-x}Ca_xP_4O_{12}$

The scheme (5) describes our procedure of the synthesis of $Mn_{2-x}Ca_xP_4O_{12}$:

$$(1 - x/2)Mn_2P_4O_{12} + x\ Ca(PO_3)_2 + 4/n\ H_2O \xrightarrow[\text{(air-wet atmosphere)}]{\text{melting (920–950°C)}}$$

$$4/n\ (Mn_{2-x}Ca_x)_{n/4}\ H_2P_nO_{3n+1(l)} \xrightarrow[\text{solidification}]{950 \to 25°C}$$

$$4/n\ (Mn_{2-x}Ca_x)_{n/4}\ H_2P_nO_{3n+1(glass)} \xrightarrow{T\ \text{recrystallization}}$$

$$Mn_{2-x}Ca_xP_4O_{12(cryst.)} + 4/n\ H_2O \quad (5)$$

The mixtures for syntheses of the binary products were prepared from the simple tetrametaphosphates starting materials whose ratio was adjusted to make x equal to 0·25, 0·5, 0·75, 1·0, 1·05, 1·1, 1·15 and 1·25. In addition, the same two-step procedure was also applied to the pure $Mn_2P_4O_{12}$ ($x = 0$) 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 1000°C, i.e. above the melting temperature of the higher-melting starting

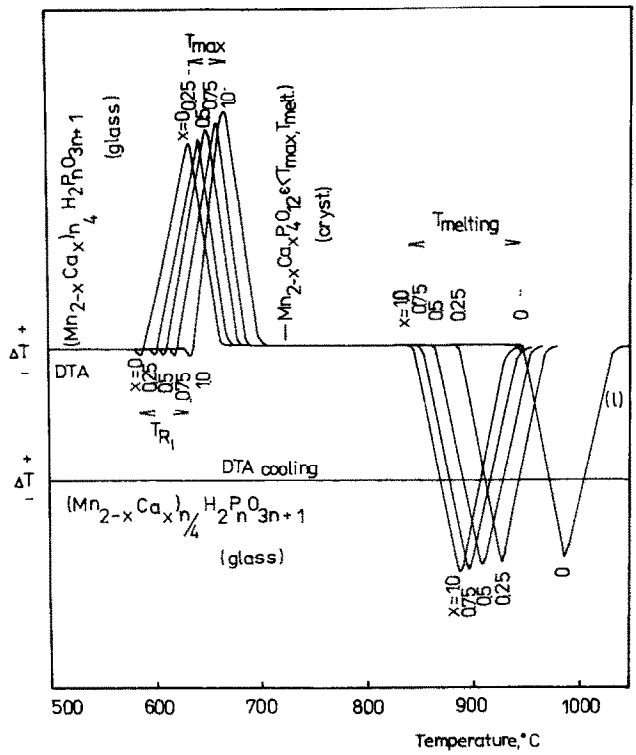

Fig. 1. The DTA curves of the vitreous intermediates $(Mn_{2-x}Ca_x)_{n/4}H_2P_nO_{3n+1}$ indicating the formation of the products $Mn_{2-x}Ca_xP_4O_{12}$ [by reaction (6)] and their incongruent melting.[7] Sample weight 15 mg.

phosphate ($Mn_2P_4O_{12}$: 950°C). After 30 min, the dishes with melts were removed from the furnace and rapidly cooled by immersion in water. The vitreous products of the higher linear phosphate type $(Mn_{2-x}Ca_x)_{n/4}H_2P_nO_{3n+1}$ were dried at 105°C and ground in a vibrating pebble mill. Other aliquots of these intermediates were then subject to DTA (Fig. 1) in order to find the temperatures of the exothermic processes of thermal recrystallization. These temperatures correspond to those of formation of the binary manganese–calcium tetrametaphosphates (Table 2,

TABLE 2
Conditions of Formation of $Mn_{2-x}Ca_xP_4O_{12}$

	$x=0$	$x=0{\cdot}25$	$x=0{\cdot}5$	$x=0{\cdot}75$	$x=1{\cdot}0$
T_{Ri} (°C)	595	604	612	625	640
T_{max} (°C)	635	645	652	658	663
$-\Delta H$ (J g^{-1})	175	179	182	184	187
Yield, α (%)	96·6	96·6	96·8	96·9	96·9

Fig. 2). Therefore, the individual intermediates were then calcinated in the electric furnace L 112.2 at temperatures 20°C higher (T_{max} + 20°C) for 30 min. The sintered blocks of the individual final products obtained in this way were ground in a vibrating pebble mill, weighed (mass m_1), and extracted with a 100-fold excess of 0·3M-HCl for 2 h; the solid was separated by filtration, dried at 105°C, and weighed (m_2).

2.3 Methods of instrumental analysis

2.3.1 Quality evaluation of the starting phosphates, intermediates and products

The evaluation was carried out by chromatography[22,23] with a TLC II set from Kavalier Sázava ČSSR, IR spectroscopy[24] with a Perkin–Elmer 684 infrared spectrophotometer, X-ray diffraction analysis[25,26] with a HZG-4 GDR. Moreover, the extraction method developed in our laboratory (the extraction with 0·3M-HCl)[21] was used: vitreous intermediates of the higher linear phosphate type are dissolved, whereas tetrametaphosphates resist the extraction. Hence, in the cases when binary tetrametaphosphates are formed without any further crystalline phase (see below) it is possible to determine the yield of recrystallization from the relationship m_2/m_1 (Section 2.2, Table 2, Fig. 2). The sample aliquots of the individual products were dissolved by boiling in 15% HCl (several days) and analysed by means of atomic

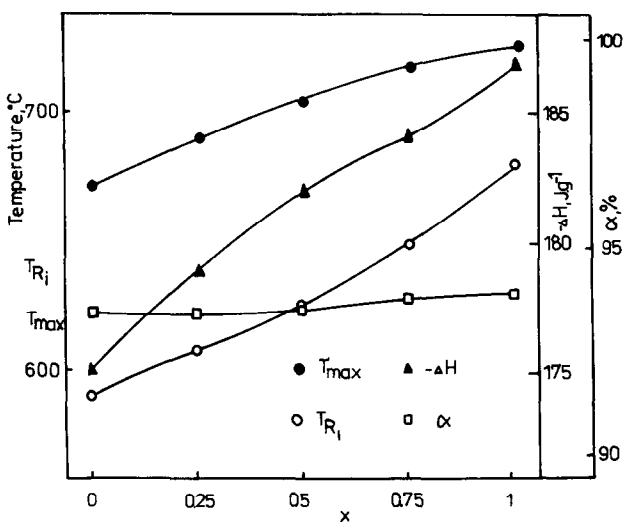

Fig. 2. Reaction (6) of formation of $Mn_{2-x}Ca_xP_4O_{12}$: dependence on the calcium content (x) of (○) T_{R_i}, the temperatures of the beginning of the reaction; (●) T_{max}, the temperatures of the maxima of exothermic effects (Fig. 1); (▲) ΔH, the heats of the process; (□) α, the yields of the process.

absorption spectrometry[27] to determine the ratios $P_2O_5/(Mn + Ca)$ and Mn/Ca.

2.3.2 Determination of structural parameters of $Mn_{2-x}Ca_xP_4O_{12}$

X-ray powder diffractograms of the samples were obtained using a vertical X-ray diffractometer HZG-4B (VEB Freiberger Präzisionsmechanik, GDR), equipped with a goniometer of 25 cm diameter and a proportional detector. CuKα radiation was used with the elimination of Kβ radiation by a nickel filter; in the range $2\theta = 10$–$35°$ the interplanar spacing was calculated using CuKα radiation ($\lambda = 0{\cdot}154\,178$ nm) and in the range $2\theta = 35$–$90°$ CuKα_1 radiation ($\lambda = 0{\cdot}154\,051$ nm) was used.

Powdered silicon ($a = 0{\cdot}543\,055$ 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 fact that the binary manganese(II)–calcium(II) tetrametaphosphates are isostructural with

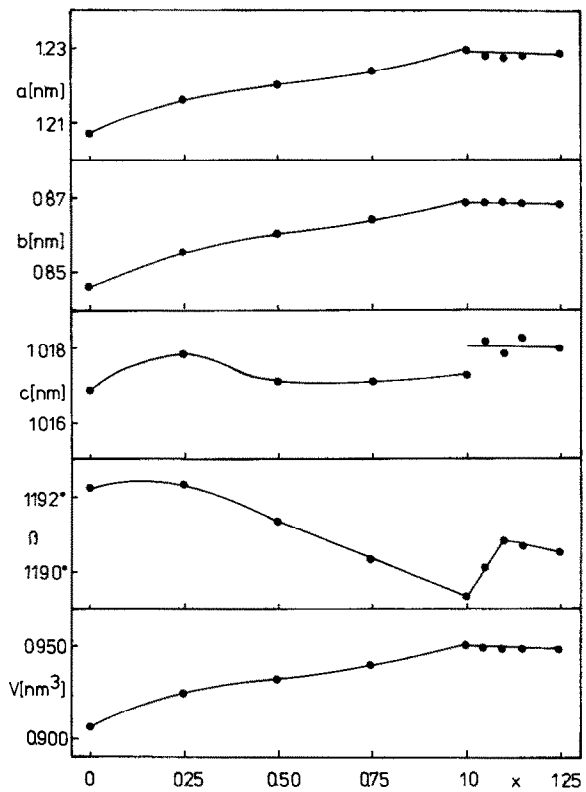

Fig. 3. The structural parameters a, b, c and β and the volume V of the elementary unit cell of $Mn_{2-x}Ca_xP_4O_{12}$.

TABLE 3
Structural Parameters of $Mn_{2-x}Ca_xP_4O_{12}$

x	$a(nm)$	$b(nm)$	$c(nm)$	β (°)	$V(nm^3)$	Δ^a	*No. of phases*
$Mn_{2-x}Ca_xP_4O_{12}$							
0	1·207 7(4)	0·846 7(3)	1·016 9(4)	119·23(2)	0·907 4	0·006	One
0·25	1·215 9(5)	0·855 5(4)	1·017 9(4)	119·14(2)	0·924 7	0·010	One
0·50	1·220 0(7)	0·860 5(6)	1·017 1(6)	119·24(4)	0·931 7	0·012	One
0·75	1·223 7(8)	0·864 4(6)	1·017 1(6)	119·04(4)	0·940 3	0·013	One
1·00	1·229 5(5)	0·868 8(4)	1·017 3(4)	118·94(3)	0·951 0	0·008	One
Mixtures							
1·05	1·227 6(4)	0·868 8(3)	1·018 2(3)	119·02(2)	0·949 6	0·006	More than one
1·10	1·227 7(5)	0·869 0(3)	1·017 9(4)	119·09(2)	0·949 0	0·007	
1·15	1·228 0(5)	0·868 6(4)	1·018 3(4)	119·07(3)	0·949 3	0·009	
1·25	1·228 4(8)	0·868 2(6)	1·018 0(6)	119·06(4)	0·949 0	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 investigated diffraction lines.

$Mn_2P_4O_{12}$, which crystallizes 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 3); their dependence on the amount of calcium in the products is presented in Fig. 3.

2.3.3 Estimation of some physical properties

The products were analysed by the pycnometric method[28] to estimate their density and by the DTA method (DTA-1700 in DSC mode, Perkin–Elmer)[29] along with high-temperature microscopy (MHO-2, Zeiss Jena) to estimate their melting points. The values found are given in Table 4, and their dependence on the amount of calcium in the products is presented in Fig. 4.

With respect to the proposed application as new anticorrosion pigments,[18] the products were also evaluated from this point of view. First we compared the corrosion of steel sheets immersed in the pigment extracts for 8 days: the extracts were prepared by extracting 10 g pigment with 90 ml

TABLE 4
Melting Points and Densities of $Mn_{2-x}Ca_xP_4O_{12}$

x	*0*	*0·25*	*0·50*	*0·75*	*1·00*
$T_{melting}$ (°C)	950	887	862	848	843
ρ_{exp} (g cm^{-3})	3·15	3·06	3·01	2·94	2·88
ρ_{calc} (g cm^{-3})	3·116	3·031	2·982	2·929	2·870

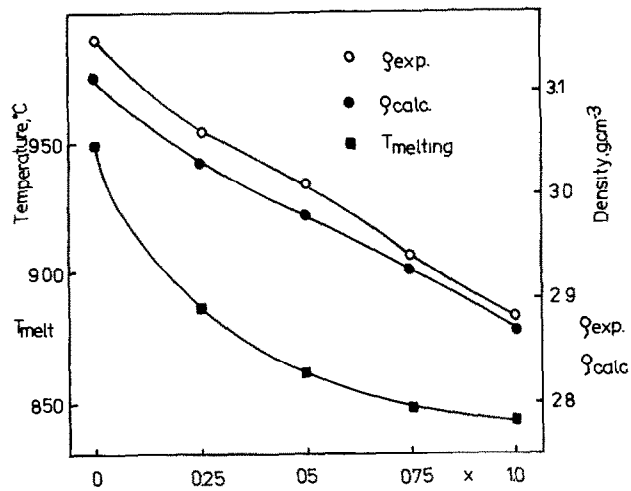

Fig. 4. The dependence of melting temperatures (■) and experimental (○) and calculated densities (●) of the products $Mn_{2-x}Ca_xP_4O_{12}$ on the calcium content (x).

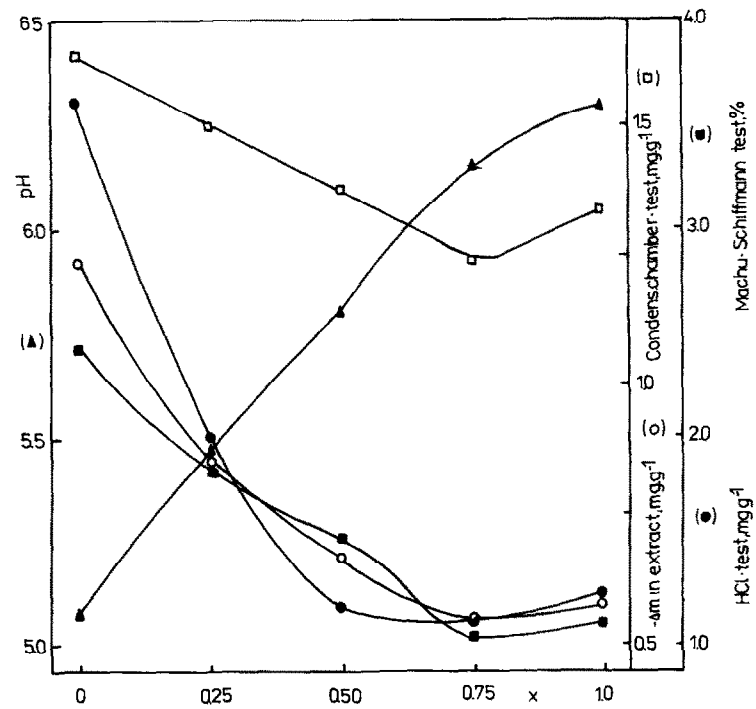

Fig. 5. Dependence of values obtained from anticorrosion tests with $Mn_{2-x}Ca_xP_4O_{12}$ on calcium content (see Tables 5 and 6). ▲, pH of extract (original); ○, loss in steel weight due to corrosion in the extract; ●, test in HCl vapour; □, test in condensation chamber: ■, test by Machu & Schiffman's method.

TABLE 5
Evaluation of the Inhibition Ability of Powdery $Mn_{2-x}Ca_xP_4O_{12}$

Pigment	*pH of aqueous extract of powdery product*			*Decrease in mass of steel*[a] ($mg\,g^{-1}$)
	Original	*Eight days after immersion of steel sheet in the extract*	*Eight days after removal of steel sheet from the extract*	
$Mn_2P_4O_{12}$	5·07	5·86	5·52	1·234
$Mn_{1.75}Ca_{0.25}P_4O_{12}$	5·48	6·05	5·73	0·860
$Mn_{1.5}Ca_{0.5}P_4O_{12}$	5·81	6·42	6·04	0·665
$Mn_{1\ 25}Ca_{0.75}P_4O_{12}$	6·15	6·78	6·32	0·543
$MnCaP_4O_{12}$	6·30	6·92	6·45	0·576
$Ca(PO_3)_2$	6·42	6·98	6·62	1·033

[a] Due to corrosion during 8 days' immersion in the aqueous extract of pigment.

distilled water for 24 h, 2 h of which were stirring.[30] Next we examined the pH changes of the pigment extracts on contact with the steel sheets.[30] Finally, we also prepared and evaluated the oil coating compositions containing our products. The compositions were prepared in a Attritor-De 034S disperser (Stephan Werke, FRG) from the following components: 29% linseed oil, 9·2% $Mn_{2-x}Ca_xP_4O_{12}$, 54% Fe_2O_3 (Bayferox 130), 6.6% talc,

TABLE 6
Evaluation of Anticorrosion Properties of Oil Coating Compositions Containing 9·2% (w/w) $Mn_{2-x}Ca_xP_4O_{12}$

Pigment	*Decrease in weight of steel*[a] *due to corrosion*		*Area of damaged coating*[b]	
	After 28 days in condensation chamber ($mg\,g^{-1}$)	*After 8 days in HCl vapour* ($mg\,g^{-1}$)	(mm^2)	(%)
$Mn_2P_4O_{12}$	1·64	3·62	22·0	2·44
$Mn_{1\ 75}Ca_{0.25}P_4O_{12}$	1·50	2·01	16·7	1·85
$Mn_{1.5}Ca_{0\ 5}P_4O_{12}$	1·38	1·17	13·7	1·52
$Mn_{1.25}Ca_{0.75}P_4O_{12}$	1·24	1·12	9·3	1·03
$MnCaP_4O_{12}$	1·34	1·25	9·8	1·09
$Ca(PO_3)_2$	1·40	1·29	11·0	1·22

[a] With application of the pigment-containing coating.
[b] Near a cut of length 100 mm; in a rapid immersion test of resistance against undercorrosion, according to Machu & Schiffman.

1·2% desiccant (1% solution of cobalt(II) octanoate in petroleum spirit). These coating compositions were applied to steel sheets and submitted to laboratory tests of protective efficiency (Tables 5, 6; Fig. 5):

(a) corrosion test in vapour of 18% hydrochloric acid for 8 days;[31]
(b) corrosion test with condensation of water vapour;[32]
(c) accelerating test of paint coatings resistance against undercorrosion (Machu & Schiffman's method).[33]

3 RESULTS AND DISCUSSION

Figure 1 represents the DTA curves of the vitreous intermediates $(Mn_{2-x}Ca_x)_{n/4}H_2P_nO_{3n+1}$ for $x = 0$, 0·25, 0·50, 0·75, 1·0 and 2·0. The first sections (up to 700°C) indicate an exothermic process. This process represents the reaction of formation of the tetrametaphosphate which is connected with the initial softening and subsequent recrystallization of the amorphous vitreous phase.[6]

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

Both the heat and temperatures of this process determined under the conditions of thermal analysis (Table 2, Fig. 2) indicate that increasing 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 also with the heat and the yield 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 (decreasing with increasing calcium content). The molar ratio $P_2O_5/(Mn + Ca)$, determined in the extracted products, varies from 0·9996 to 1·0005, and the mutual ratio of the divalent metals, Mn/Ca, corresponds very precisely to the values $(2 - x)/x$. The instrumental analytical methods confirmed that each product represents only a single phase, and the composition of its anion corresponds to tetrametaphosphate. Therefrom it follows that the two-step synthesis described succeeded in giving products of the type of binary manganese(II)–calcium(II) tetrametaphosphates of formula $Mn_{2-x}Ca_xP_4O_{12}$. However, the X-ray diffraction analysis showed that no binary products are formed within the whole range of x (Table 3).

The dependence of the lattice parameters and volume of the elementary cell on the proportion of the Ca(II) component in the product are given in Fig. 3. It is evident that the volume of the elementary cell of the double tetrametaphosphate is increased with the Ca(II) content, which agrees with the fact that its radius is greater than that of Mn(II) by about one-fifth. At the molar ratio of Mn/Ca = 1 in the product, there appears a break in the

dependences 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 are practically no longer changed. The diffractograms then exhibit lines of a further phase. The results thus indicate that it is possible to prepare double Mn(II)–Ca(II) tetrametaphosphates with the molar ratio of Ca/Mn ≤ 1. Hence, the existence of this type of product with 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) tetrametaphosphate as already noted in the Introduction.)

Some physical properties of the products determined with respect to their potential application as pigments are summarized in Table 4. As the yields of this synthesis were high, the sections of the DTA curves above the recrystallization temperature can be considered as determining the thermal stabilities of the binary tetrametaphosphates. The endothermic effects at these DTA curves document their melting (as was confirmed by high-temperature microscopy) which is incongruent: the tetrametaphosphates are transformed into higher linear phosphates,[7] which is favoured by the presence of at least traces of water vapour in the air atmosphere.[34]

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

Hence, in these conditions the melting points represent the temperatures up to which the binary tetrametaphosphates are stable; with the calcium content they decrease from 950 to 843°C (Fig. 4). This fact confirms the high thermostability of the products, which extends the range of their applications to high-temperature purposes.

Also, the density of the binary products continuously changes with the calcium content. However, according to expectation, in this case the density values decrease with increasing x [which again agrees with the lower density found for $Ca(PO_3)_2$ as compared with that found for the pure $Mn_2P_4O_{12}$], 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 results of the laboratory tests on protective efficiency showed the effect of the binary Mn–Ca tetrametaphosphates in the sense of anticorrosion-inhibition activity (Tables 5 and 6). Most values are distinctly better than those obtained with reference samples containing a commercial anticorrosion pigment of the type of simple zinc(II) phosphate dihydrate [$Zn_3(PO_4)_2 . 2H_2O$].[35] This result is caused by the higher content of the phosphoric component in tetrametaphosphates 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 humid medium[5,18] (after gradual splitting of the cyclic tetraphosphate anion[6]). A certain anticorrosion-inhibition

action of manganese(II) ions[36] represents an additional favourable factor. The presence of calcium(II) ion in addition causes an alkalinity increase (or better, acidity lowering) of the binary products (see the pH values in Table 5), which again favourably affects the anticorrosion-inhibition ability. Therefore, the binary manganese(II)–calcium(II) tetrametaphosphates proved to be more efficient than the pure manganese(II) tetrametaphosphate (Fig. 5) and the corresponding calcium derivative.[5] Also, it is obvious that there exists a certain optimum with regard to the calcium content in these binary products $Mn_{2-x}Ca_xP_4O_{12}$ with $0 \leq x \leq 1$: optimum lies near $x = 0{\cdot}75$ (see the minima on the curves in Fig. 5).

4 CONCLUSION

Our communication shows that it is possible to prepare binary manganese(II)–calcium(II) tetrametaphosphates $Mn_{2-x}Ca_xP_4O_{12}$, where $0 \leq x \leq 1$. (However, the existence of this type of product with the Ca/Mn molar ratio above 1 cannot be expected.) The products crystallize in the monoclinic system, *C2c* group. Their structural parameters have the values: $a = 1{\cdot}2007$–$1{\cdot}2295$ nm, $b = 0{\cdot}8467$–$0{\cdot}8688$ nm, $c = 1{\cdot}0169$–$1{\cdot}0173$ nm, $\beta = 118{\cdot}94°$–$119{\cdot}24°$ (the volume of elementary cell increases from $0{\cdot}9074\,nm^3$ to $0{\cdot}9510\,nm^3$ with increasing proportion of calcium in the product). The melting temperatures and densities decrease with decreasing calcium content (the respective intervals are 950–843°C and $3{\cdot}15$–$2{\cdot}88\,g\,cm^{-3}$).

The binary manganese(II)–calcium(II) tetrametaphosphates $Mn_{2-x}Ca_xP_4O_{12}$ exhibit very good anticorrosion-inhibition properties; their maximum value is obviously reached in the product of Mn/Ca molar ratio near 1·67.

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