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Binary Cyclotetraphosphates $Co_{2-x}Ni_xP_4O_{12}$ and $Mn_{2-x}Ni_xP_4O_{12}$ as Colour Thermostable Products

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ABSTRACT

Cyclotetraphosphates (tetrametaphosphates) of the type $Co_{2-x}Ni_xP_4O_{12}$ *and* $Mn_{2-x}Ni_xP_4O_{12}$*, where* $x \in (0; 2)$*, 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. Temperatures 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; yields increase with increasing* x *(the nickel content). The structure of the products and the structural parameters have been determined. With respect to the proposed application of these products as special inorganic pigments, the density, thermal stability and colour of the compounds were determined.*

1 INTRODUCTION

Binary cobalt(II)–nickel(II) and manganese(II)–nickel(II) tetraphosphates with cyclic anions have not been described in the literature and recent reviews[1–3] make no reference to them.

The procedure suggested by us for the preparation of binary cobalt–nickel and manganese–nickel cyclotetraphosphates[4] and documented in this present paper is based on a two-step thermal synthesis. The first step starts from pure cyclotetraphosphates of the two divalent metals which are melted and then abruptly cooled to give a vitreous amorphous product composed of higher linear phosphates of the general formula $(Co_{2-x}Ni_x)_{n/4}H_2P_nO_{3n+1}$ or $(Mn_{2-x}Ni_x)_{n/4}H_2P_nO_{3n+1}$.[5] In the second step this product is repeatedly

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heated to a suitable temperature and recrystallized to give a microcrystalline product $Co_{2-x}Ni_xP_4O_{12}$ or $Mn_{2-x}Ni_xP_4O_{12}$. We have synthesized these cyclotetraphosphates of divalent metals[6,7] and evaluated them with respect to their application as special inorganic pigments for high-temperature ceramic,[8,9] anti-corrosion[10,11] and luminescence purposes.[12,13] The object of the preparation of the binary products is to improve the properties of the pigments with respect to these applications.[14]

2 EXPERIMENTAL PROCEDURE

2.1 Preparation of the starting cyclotetraphosphates $Co_2P_4O_{12}$, $Mn_2P_4O_{12}$ and $Ni_2P_4O_{12}$

The simple cyclotetraphosphate starting materials were prepared on the basis of the previously described thermal method,[15] modified[16] so as to obtain the cyclotetraphosphates as pure as possible.

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

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

$$2MH_2P_2O_7 \xrightarrow{T_3} M_2P_4O_{12} + 2H_2O \quad (3)$$

$$(M^{II} = Co, Mn, Ni)$$

The temperatures of the individual reactions are shown in Table 1; the underlined temperatures being those at which the calcination of forming cyclotetraphosphates was performed. The carbonates of the individual metals and the 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 eqn (1) were calcinated separately in an electric muffle furnace (L 112.2, VEB Frankenhausen, GDR). The rate of temperature

TABLE 1
The Temperatures (°C) of the Individual Reactions (1)–(3) in the Synthesis of $Co_2P_4O_{12}$, $Mn_2P_4O_{12}$ and $Ni_2P_4O_{12}$

Me	T_1	T_2	T_3
Co	105–$\underline{180}$	180–$\underline{240}$	280–$\underline{295}$
Mn	$\underline{120}$	$\underline{205}$	$\underline{310}$
Ni	$\underline{130}$	195–$\underline{250}$	$\underline{370}$

$(pH_2O_{(g)} \rightarrow 100\,kPa)$

increase was 2°C min^{-1}, the temperatures T_1, T_2 and T_3 being maintained for 60 min each. The final calcination was carried out 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 cyclotetraphosphates were purified by extraction with 0·3M-HCl to remove all the side-products.[17]

2.2 Preparation of $Co_{2-x}Ni_xP_4O_{12}$ and $Mn_{2-x}Ni_xP_4O_{12}$

The synthesis is outlined in the scheme of reactions (4)

$$\begin{aligned}&\left(1-\frac{x}{2}\right)Me_2P_4O_{12(cryst)}+\frac{x}{2}Ni_2P_4O_{12(cryst.)}\\&\qquad+\frac{4}{n}H_2O \xrightarrow[\text{(wet-air-atmosphere)}]{\text{melting}(T_{melt}(Me_2P_4O_{12})\simeq 1250^\circ C)}\\&\qquad\frac{4}{n}(Me_{2-x}Ni_x)_{n/4}H_2P_nO_{3n+1(l)} \xrightarrow[\text{(solidification)}]{1250\to 25^\circ C}\\&\qquad\frac{4}{n}(Me_{2-x}Ni_x)_{n/4}H_2P_nO_{3n+1(glass)} \xrightarrow{T_{recrystallization}}\\&\qquad Me_{2-x}Ni_xP_4O_{12(cryst)}+\frac{4}{n}H_2O\end{aligned}\tag{4}$$

[Me = Co or Mn; $T_{melt}(Me_2P_4O_{12}) = 1060^\circ C(Co_2P_4O_{12})$, 950°C $(Mn_2P_4O_{12})$]

The mixtures for the syntheses of the binary products were prepared from the cyclotetraphosphates with ratio adjusted to make the x value equal to 0·25, 0·5, 0·75, 1·0, 1·25, 1·5 and 1·75. In addition, the same two-step procedure was also applied to pure $Co_2P_4O_{12}$ and $Mn_2P_4O_{12}$ ($x = 0$) and pure $Ni_2P_4O_{12}$ ($x = 2$). The mixtures were homogenized in an agate mortar and then melted on platinum dishes in an electric furnace by heating to 1300°C, i.e. above the melting temperature of the higher-melting starting cyclotetraphosphate ($Ni_2P_4O_{12}$: 1250°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 type of higher linear phosphates $(Co_{2-x}Ni_x)_{n/4}H_2P_nO_{3n+1}$ or $(Mn_{2-x}Ni_x)_{n/4}H_2P_nO_{3n+1}$ were dried at 120°C and ground in a vibrating pebble mill. (The quality of these intermediates was checked by instrumental analytical methods which proved their homogeneity, amorphous character and the presence of long linear chains of the anions; sample aliquots were treated with 0·3M-HCl and dissolved completely, confirming that the intermediates did not contain any residual starting cyclotetraphosphates.) Other aliquots of these intermediates were then subjected to DTA (apparatus DTA 1700/DSC mode, Perkin–Elmer[18]) in order to ascertain the temperatures of the exothermic processes of thermal recrystallization (Fig. 1). These temperatures correspond to those of formation of the binary cobalt–nickel cyclotetraphosphates or manganese–nickel cyclotetraphosphates (Table 2, Fig. 2); therefore, the individual intermediates were then calcinated at temperatures 20°C higher ($T_{max} + 20°C$) for 30 min. The sintered blocks of the final products thus obtained were ground in a vibrating pebble mill. The yields of the process (α) were determined by the special analytical extraction method.[17]

2.3 Evaluation of products and intermediates

The cyclotetraphosphates, vitreous amorphous intermediates and final products were analyzed by chromatography,[19] IR spectroscopy,[20] X-ray diffraction analysis[21] and atomic absorption spectrometry. The products were also investigated using X-ray powder diffraction ($\lambda Cu_{K\alpha} = 0{\cdot}154\,178$ nm).[22] The diffractograms were indexed under the presumption that the binary cyclotetraphosphates are isostructural with $Co_2P_4O_{12}$, $Mn_2P_4O_{12}$ and $Ni_2P_4O_{12}$;[21] the lattice parameters of the monoclinic elementary cell ($C2c$ group) were calculated by the least-squares treatment (Table 3; Fig. 3).

The products were also evaluated by the pycnometric method to estimate their density and by the DTA method[18] and high-temperature microscopy (MHO-2, Zeiss–Jena) to estimate their melting temperatures (Table 4; Fig. 4) and the measured reflectance factor (Specol 10, Zeiss–Jena) in the visible light region (Fig. 5).

3 RESULTS AND DISCUSSION

Figure 1 shows the DTA curves, whose first sections indicate an exothermic process. This process represents the reaction of formation of the binary cyclotetraphosphate from intermediates of the higher linear phosphate type (5), and is connected with recrystallization of the amorphous vitreous phase.

$$(Me_{2-x}Ni_x)_{n/4}H_2P_nO_{3n+1(glass)} \rightarrow \frac{n}{4} Me_{2-x}Ni_xP_4O_{12(cryst)} + H_2O_{(g)}$$

$$(Me = Co, Mn) \qquad (5)$$

Both the temperatures of this process determined under the conditions of thermal analysis (Table 2; Fig. 2) indicate that increasing nickel content is connected with a continuous increase of both the temperature of the

TABLE 2

The Conditions of Formation of $Co_{2-x}Ni_xP_4O_{12}$ and $Mn_{2-x}Ni_xP_4O_{12}$ [reaction (5)]

		0	*0·25*	*0·5*	*0·75*	*1·0*	*1·25*	*1·5*	*1·75*	*2·0*
T_{R_1} (°C)	Co–Ni	635	656	676	698	712	725	740	752	776
	(Mn–Ni)	(550)	(582)	(613)	(643)	(670)	(688)	(707)	(725)	(776)
T_{max} (°C)	Co–Ni	673	690	710	735	742	758	770	787	790
	(Mn–Ni)	(583)	(615)	(642)	(674)	(695)	(717)	(730)	(760)	(796)
Yield, α (%)	Co–Ni	98·20	98·25	98·34	98·45	98·47	98·52	98·58	98·60	98·70
	(Mn–Ni)	(96·60)	(96·65)	(96·80)	(97·15)	(97·50)	(97·90)	(98·10)	(98·32)	(98·60)

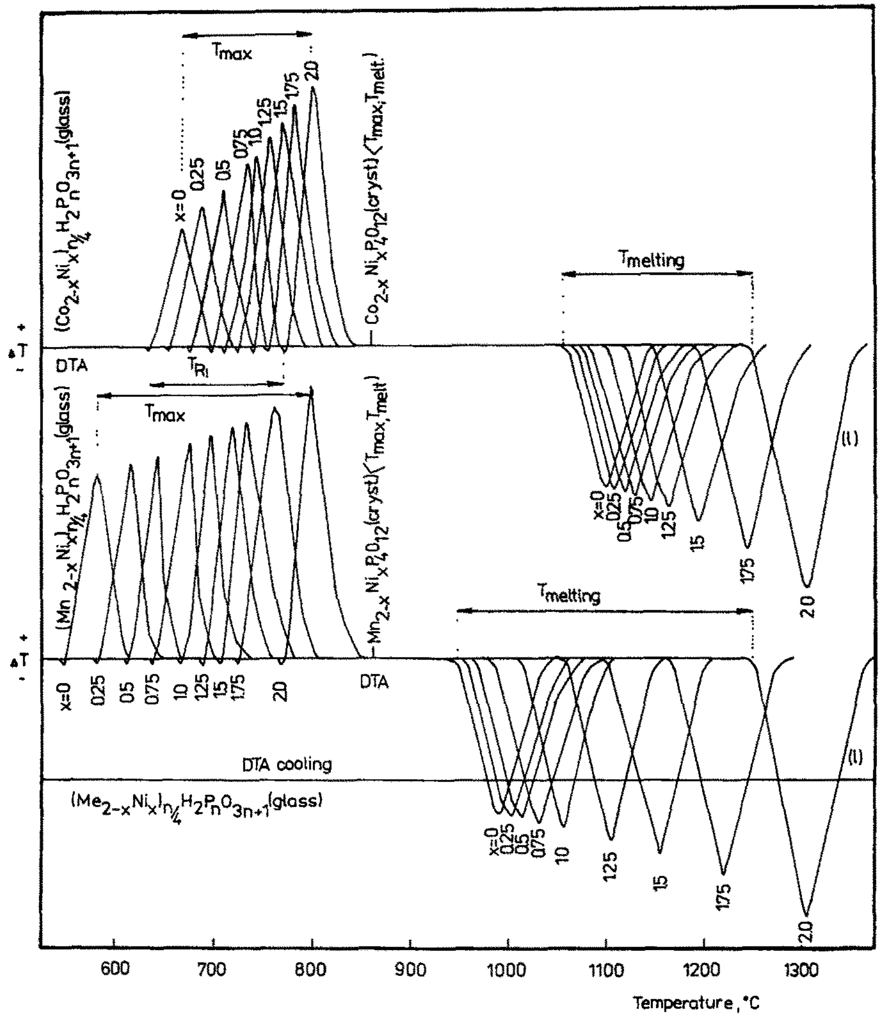

Fig. 1. The DTA curves of the vitreous intermediates $(Co_{2-x}Ni_x)_{n/4}H_2P_nO_{3n+1}$ and $(Mn_{2-x}Ni_x)_{n/4}H_2P_nO_{3n+1}$ indicating the formation of the products $Co_{2-x}Ni_xP_4O_{12}$ or $Mn_{2-x}Ni_xP_4O_{12}$ [by reaction (5)] and the changes in the melting characteristics [reaction (6)]. Sample weight: 15 mg; temperature increase: 20°C min^{-1}; platinum crucible (open); atmosphere, air.

beginning [T_{Ri}; in the interval 635–776°C (Co–Ni) or 550–776°C (Mn–Ni)) and the temperature of the maximum exothermic effects (T_{max}; 673–796°C (Co–Ni) or 583–796°C (Mn–Ni))].

Analysis of the products prepared on a larger scale in electric furnaces at the temperatures T_{max} + 20°C showed that the yields are high and increase with increasing nickel content. The molar ratio $P_2O_5/(Me + Ni)$ determined in the extracted products varied from 0·9995 to 1·0008 (Co–Ni) and 0·9992 to

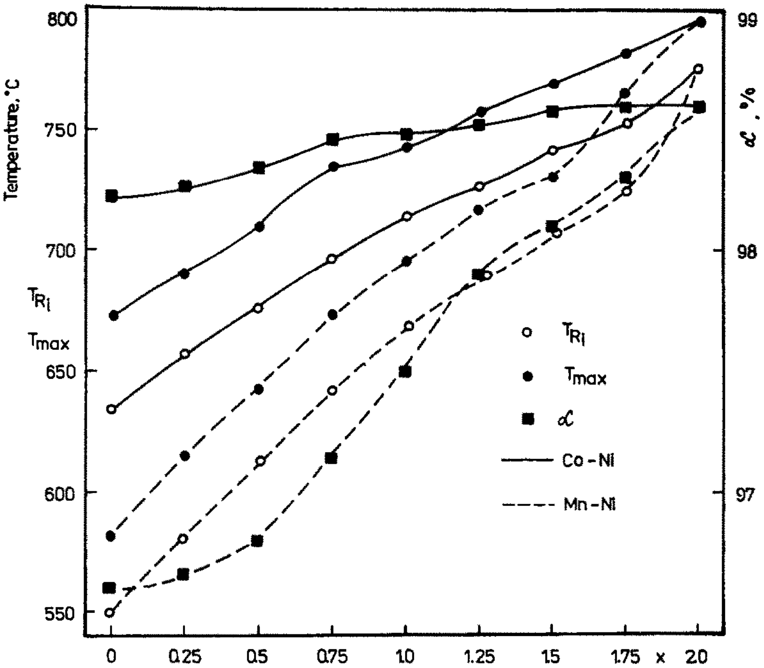

Fig. 2. The values for the reaction (5) of formation of $Co_{2-x}Ni_xP_4O_{12}$ (——) and $Mn_{2-x}Ni_xP_4O_{12}$ (- - -), showing the dependence on the nickel content (x) of (○) T_{R_I}, the temperature of the beginning of the reaction; (●) T_{max}, the temperature of the maximum of exothermic effects (Fig. 1); and (■) α, the yield of the process.

1·0012 (Mn–Ni); the mutual ratio of the divalent metals, Co/Ni and Mn/Ni, 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 cyclotetraphosphate. Therefore it follows that the two-step synthesis did give products of the binary cobalt(II)–nickel(II) cyclotetraphosphate and binary manganese(II)–nickel(II) cyclotetraphosphate type of formula $Co_{2-x}Ni_xP_4O_{12}$, $Mn_{2-x}Ni_xP_4O_{12}$, a conclusion applicable to the whole range of $x \in (0;2)$.[23]

The structural parameters of the products (Table 3; Fig. 3) are slowly but distinctly changed with changing nickel content. Their values lie in the intervals limited by the structural parameters of the pure simple cyclotetraphosphates $Co_2P_4O_{12}$ and $Ni_2P_4O_{12}$ or $Mn_2P_4O_{12}$ and $Ni_2P_4O_{12}$. The volume of the primitive unitcell of the binary products decreases regularly with increasing nickel content in accord with the smaller ionic radius of nickel compared with cobalt and manganese.

Some physical characteristics of the products determined with respect to

TABLE 3
The Structural Parameters of $Co_{2-x}Ni_xP_4O_{12}$ and $Mn_{2-x}Ni_xP_4O_{12}$

Parameter		*x*								
		0	*0·25*	*0·5*	*0·75*	*1·0*	*1·25*	*1·5*	*1·75*	*2·0*
a (nm)	Co–Ni	1·179 9(5)	1·177 9(6)	1·175 9(5)	1·174 6(6)	1·172 7(5)	1·170 8(7)	1·168 9(6)	1·166 9(7)	1·164 4(5)
	Mn–Ni	1·207 6(4)	1·201 7(8)	1·196 4(8)	1·192 0(5)	1·187 2(7)	1·178 7(7)	1·172 4(8)	1·168 1(5)	1·164 4(5)
b (nm)	Co–Ni	0·830 4(4)	0·830 2(5)	0·829 4(4)	0·828 7(5)	0·827 6(4)	0·826 6(5)	0·825 8(5)	0·825 1(6)	0·823 8(4)
	Mn–Ni	0·848 4(3)	0·847 3(6)	0·844 2(6)	0·841 3(4)	0·839 3(5)	0·833 6(6)	0·829 2(6)	0·826 9(4)	0·823 8(4)
c (nm)	Co–Ni	0·988 7(4)	0·987 3(5)	0·986 1(4)	0·985 3(5)	0·985 0(4)	0·984 3(5)	0·984 1(4)	0·982 6(6)	0·981 3(4)
	Mn–Ni	1·015 2(3)	1·007 0(6)	1·003 3(6)	0·997 4(4)	0·994 7(5)	0·989 0(6)	0·986 0(6)	0·984 0(4)	0·981 3(4)
β (°)	Co–Ni	118·70(3)	118·66(3)	118·61(2)	118·61(3)	118·56(3)	118·52(3)	118·54(3)	118·52(3)	118·53(2)
	Mn–Ni	119·32(2)	119·14(3)	118·94(3)	118·80(2)	118·69(3)	118·63(3)	118·56(3)	118·53(2)	118·53(2)
V (nm^3)	Co–Ni	0·849 7	0·847 1	0·844 3	0·842 0	0·839 7	0·836 9	0·834 5	0·831 4	0·827 0
	Mn–Ni	0·906 8	0·895 5	0·886 8	0·875 6	0·869 4	0·853 7	0·841 5	0·834 9	0·827 0
Δ^a	Co–Ni	0·013	0·015	0·014	0·014	0·013	0·015	0·012	0·019	0·011
	Mn–Ni	0·009	0·016	0·016	0·012	0·010	0·016	0·017	0·009	0·011

[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.

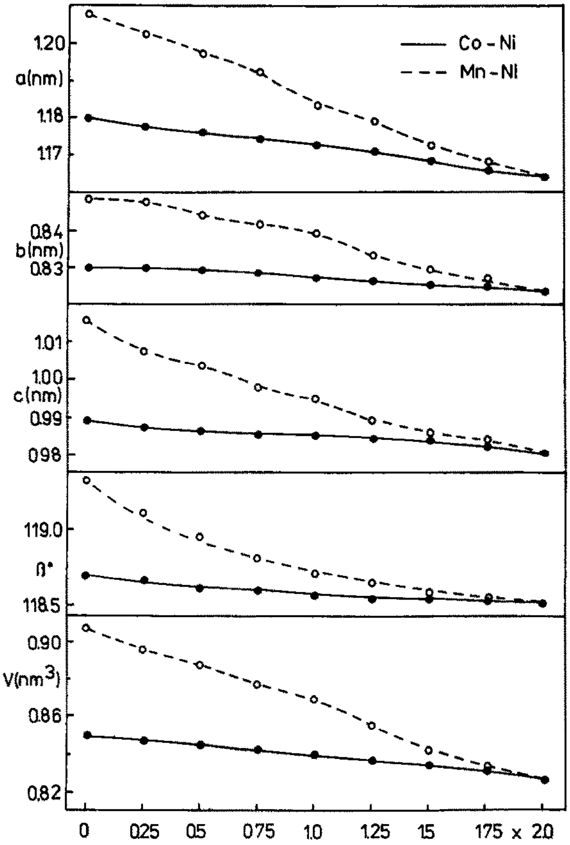

Fig. 3. The structural parameters *a*, *b*, *c* and *β* and the volume *V* of the primitive unit cell of $Co_{2-x}Ni_xP_4O_{12}$ (——) and $Mn_{2-x}Ni_xP_4O_{12}$ (– – –).

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 cyclotetraphosphates. The endothermic effects on these DTA curves indicate their variable melting (as was confirmed by means of high-temperature microscopy): the cyclotetraphosphates are transformed into higher linear phosphates [reaction (6)], a process favoured by the presence of at least traces of water vapour in the air atmosphere.

$$Me_{2-x}Ni_xP_4O_{12(cryst)} + \frac{4}{n}H_2O_{(g)} \rightarrow \frac{4}{n}(Me_{2-x}Ni_x)_{n/4}H_2P_nO_{3n+1(l)}$$

$$(Me = Co, Mn) \qquad (6)$$

Hence, at these conditions the melting temperatures represent the temperatures up to which the binary cyclotetraphosphates are stable; with

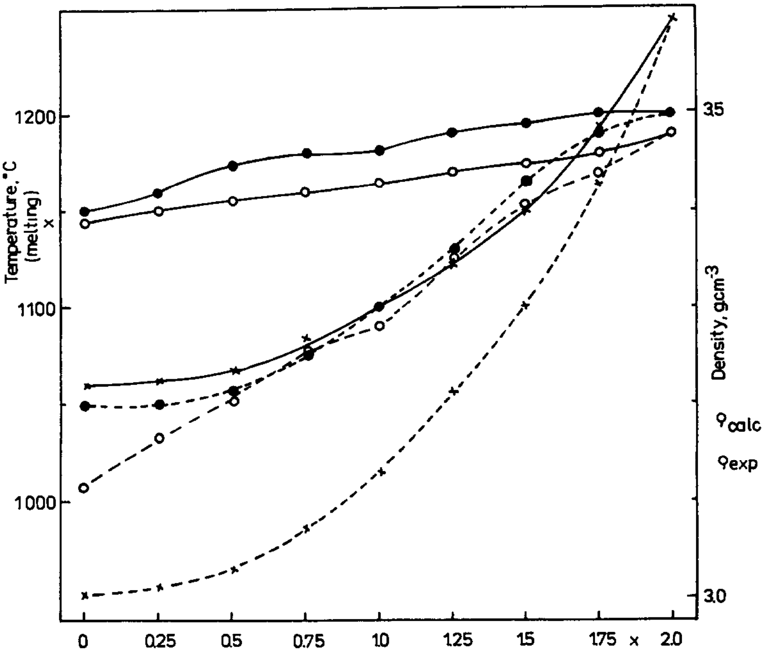

Fig. 4. The dependence on x of melting temperatures (×) and experimental (●) and calculated (○) densities of the products $Co_{2-x}Ni_xP_4O_{12}$ (——) and $Mn_{2-x}Ni_xP_4O_{12}$ (– – –).

the nickel content they increase from 1060 to 1250°C (Co–Ni) and from 950 to 1250°C (Mn–Ni) (Fig. 4). This fact indicates the high thermostability of the products, which extends the range of their application to high-temperature purposes.

The density of the binary products also changes with the nickel content, the values increasing with increasing x. The experimental values (ρ_{exp}) are in accord with the values calculated (ρ_{calc}) on the basis of the X-ray diffraction analysis (Table 4; Fig. 4).

TABLE 4

Melting Temperatures and Densities of $Co_{2-x}Ni_xP_4O_{12}$ and $Mn_{2-x}Ni_xP_4O_{12}$

		x								
		0	*0·25*	*0·5*	*0·75*	*1·0*	*1·25*	*1·5*	*1·75*	*2·0*
T_{melt}	Co–Ni	1 060	1 063	1 070	1 084	1 100	1 120	1 150	1 193	1 250
(°C)	Mn–Ni	950	955	965	985	1 015	1 057	1 100	1 164	1 250
ρ_{exp}	Co–Ni	3·40	3·42	3·46	3·46	3·46	3·48	3·49	3·50	3·50
($g cm^{-3}$)	Mn–Ni	3·20	3·20	3·21	3·25	3·30	3·36	3·43	3·48	3·50
ρ_{calc}	Co–Ni	3·391	3·401	3·411	3·420	3·429	3·440	3·450	3·462	3·480
($g cm^{-3}$)	Mn–Ni	3·116	3·165	3·203	3·251	3·282	3·349	3·405	3·405	3·480

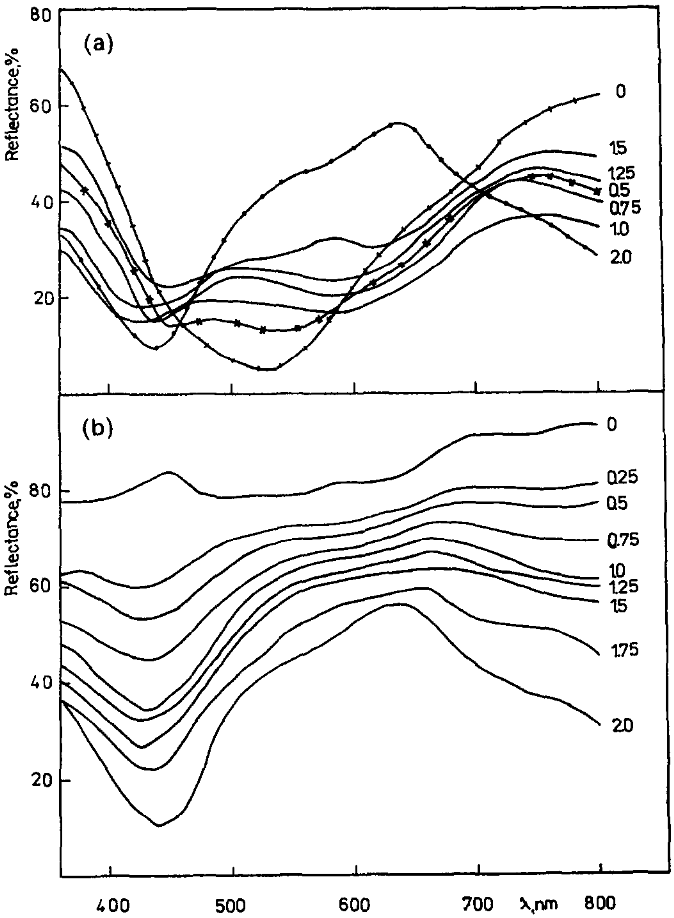

Fig. 5. The colour of the products $Co_{2-x}Ni_xP_4O_{12}$ (a) and $Mn_{2-x}Ni_xP_4O_{12}$ (b), expressed by their reflectance factor curves. The x values are indicated on the figures.

The colour of the binary cobalt(II)–nickel(II) cyclotetraphosphates is an intense blue–violet or blue–violet–brown and blue–violet–green (Fig. 5a). The colour of the binary manganese(II)–nickel(II) cyclotetraphosphates is an intense yellow or yellow–green (Fig. 5b).

4 CONCLUSION

It is shown that it is possible to prepare binary cobalt(II)–nickel(II) cyclotetraphosphates $Co_{2-x}Ni_xP_4O_{12}$ and binary manganese(II)–nickel(II) cyclotetraphosphates $Mn_{2-x}Ni_xP_4O_{12}$, where $x \in (0;2)$. These intensely coloured products crystallize in the monoclinic system, in the $C/2c$ group;

structural parameters slowly decrease with increasing nickel content. The high thermostability of the products gives the possibility of their application as high-temperature pigments.

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