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Dedicated to Professor Ferenc Paulik on the occasion of his 75th birthday

UTILIZATION OF DERIVATOGRAPH FOR STUDY OF SYNTHESIS OF NEW INORGANIC PIGMENTS

M. Trojan, P. Šulcová and D. Brandová[1]

Department of Inorganic Technology, Faculty of Chemical Technology, University of Pardubice, Legions Sq. 565, 532 10 Pardubice, Czech Republic
[1]University of Zürich, Winterthurerstrasse 190, 8057 Zürich, Switzerland

Abstract

In our laboratory, the synthesis of new inorganic pigments is followed by thermal analysis using a Derivatograph apparatus. The first information about the temperature region of the formation of the pigments investigated is provided by thermal analysis. The main attention is directed to the preparation of high-temperature colour pigments, lightfastness colour pigments, anticorrosive pigments, new ecological inorganic pigments and luminescent pigments. All inorganic pigments are useful for colouring of ceramic glazes, enamels, plastics, paints, cements and other building systems. The synthesis of all these pigments is based on temperature calcination of starting materials. Tens of new inorganic pigments have been prepared thanks to methods of thermal analysis. These synthesis are described in more than 100 Czech patents.

Keywords: anticorrosive pigments, condensed phosphate, cyclo-tetraphosphate, derivatograph, high-temperature pigments, quasi-isothermal-isobaric conditions

Introduction

The thermal analysis was carried out with instruments of type Derivatograph. Three types of this instrument are in our laboratory, i.e. Derivatograph Q-1000, Derivatograph 1500-D and Derivatograph-C. Paulik has taken part in construction of these instruments for thermal analysis. Our department has been become prominent workplace at research and development of new inorganic pigments because of consistent use of the instruments for thermal analysis.

There are main preferences of these types of Derivatographs. Simplicity of apparatus (Derivatograph Q-1000 and 1500-D) allows easy reparation and adaptation of these instruments. Sizable bulk of these instruments is also of great importance for the development of new inorganic pigments what admits to work with the weighed amount of sample up to 1.5 g (after adaptation of crucible up to 5 g). The thermal analysis can be stopped at arbitrary temperature. The interme-

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diates and the pigments obtained in this way (at sufficient amount) were studied by X-ray diffraction analysis, confirming crystalline character. These instruments of thermal analysis can be used for interpretation of principles of thermal analysis to students.

The instruments can be also used for thermal analysis under quasi-isothermal and quasi-isobaric conditions. Quite new information about thermal analyses of condensed phosphates was detected on the basis of Q-TA results. Their existence has been proved. This information was used for synthesis of many condensed phosphates as new compounds. Thermal analysis under quasi-isothermal and quasi-isobaric conditions allows synthesis of new condensed phosphates.

Modern and fast measurements of thermal analysis were carried out with Derivatograph-C apparatus that allows the evaluation of data and simultaneous registration of the thermoanalytical curves. The combination of Derivatograph-C (small weight of sample, fast reading, calculation of kinetic parameters), and Derivatograph type 1500-D and Q-1000 (the weighed amount of sample up to 5 g, quasi-isothermal-isobaric conditions) seems to be interesting for research and development of new inorganic pigments.

The increasing need of pigments, longing of people for new interesting colours of pigments and the fact that the most of the pigments contains elements (lead, chromium, antimony, cadmium, selenium), which are questionable from the hygienic point of view (environmental regulations since 1980), opens the great necessity for development and investigation of new ecological pigments. For this reason the main attention has been directed to the preparation of new compounds that would be found useful as colour environmentally friendly pigments.

Results and discussion

General

Many compounds [1], which can be used as pigments, are studied in our laboratory. The methods of thermal analysis are of a great importance for study of synthesis of condensed phosphates. The binary cyclo-tetraphosphates and the binary linear polyphosphates have been prepared on the base of results of structural parameters and chemical properties. Two methods of preparation of condensed phosphates can be used for their synthesis.

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

The second method for synthesis of condensed phosphates consists in high-temperature calcination. This procedure is based on a two-step thermal synthe-

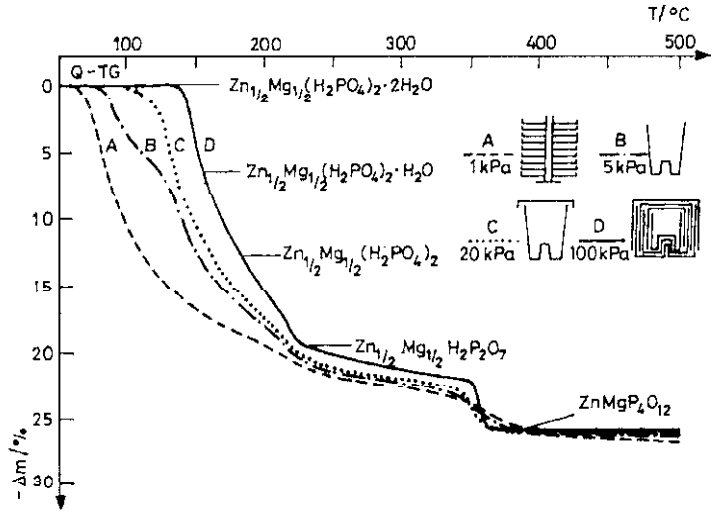

Fig. 1 Thermogravimetric curves of $Zn_{0.5}Mg_{0.5}(H_2PO_4)_2 \cdot 2H_2O$ under quasi-isothermal, quasi-isobaric conditions in air. Apparatus: Derivatograph Q-1500; sample mass: 200 mg; A – multi-plate crucible, $p_{H_2O(g)}$=1 kPa; B – opened crucible $p_{H_2O(g)}$=5 kPa; C – crucible with a lid, $p_{H_2O(g)}$=20 kPa; D – labyrinth crucible, $p_{H_2O(g)}$=100 kPa

sis. The first step, starting from the cyclo-tetraphosphates of the two bivalent metals, involves their melting in a normal air atmosphere and then abruptly cooling to give a vitreous amorphous product composed of higher linear phosphates. In the second step this product is repeatedly heated to a suitable temperature and recrystallized to give the microcrystalline product. On the base of this method new high-temperature pigments have been prepared.

The binary cyclo-tetraphosphates as new anticorrosive pigments

The thermal analysis under quasi-isothermal-isobaric conditions has been used for study of synthesis of the binary cyclo-tetraphosphates [2]. There were prepared the binary cyclo-tetraphosphates of the summary formula *c*-$M_{2-x}Me_xP_4O_{12}$ where $0<x<2$ (*M*, *Me*=bivalent metals). New anticorrosive pigments based on the cyclo-tetraphosphates doped by Zn, Mn, Co, Ca and Mg have been synthesized.

From the thermoanalytical curves (Q-TGs on Figs 1, 2 and 3) indicating formation of *c*-$ZnMgP_4O_{12}$, *c*-$MnMgP_4O_{12}$ and *c*-$CoMgP_4O_{12}$, it was found that the water vapour pressure has a great influence on the course of these condensation reactions, as well as on the temperature and velocity of the reactions, and on their results. The yield of the final pigments is sufficient high (98% of *c* $ZnMgP_4O_{12}$, 97% of *c*-$MnMgP_4O_{12}$, 98% of *c*-$CoMgP_4O_{12}$) at the water vapour pressure of about 100 kPa (using a labyrinth crucible).

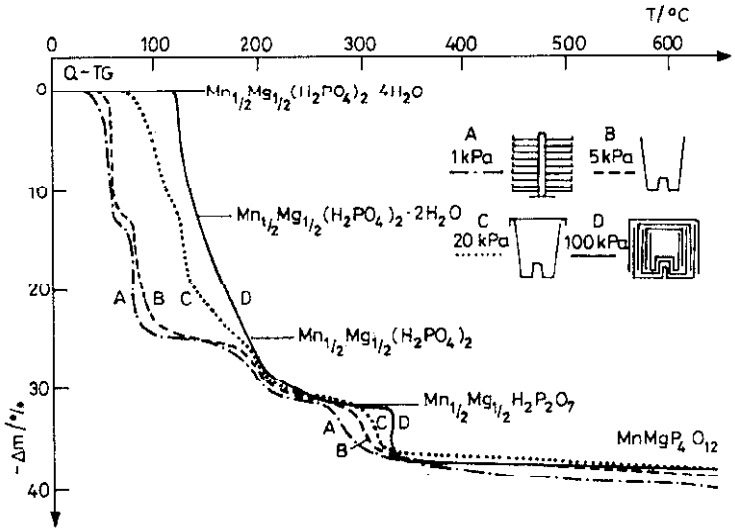

Fig. 2 Thermogravimetric curves of $Mn_{0.5}Mg_{0.5}(H_2PO_4)_2 \cdot 4H_2O$ under quasi-isothermal, quasi-isobaric conditions in air. Apparatus: Derivatograph Q-1500; sample mass, 200 mg; A – multi-plate crucible, $p_{H_2O(g)}$=1 kPa; B – opened crucible, $p_{H_2O(g)}$=5 kPa; C – crucible with a lid, $p_{H_2O(g)}$=20 kPa; D – labyrinth crucible, $p_{H_2O(g)}$=100 kPa

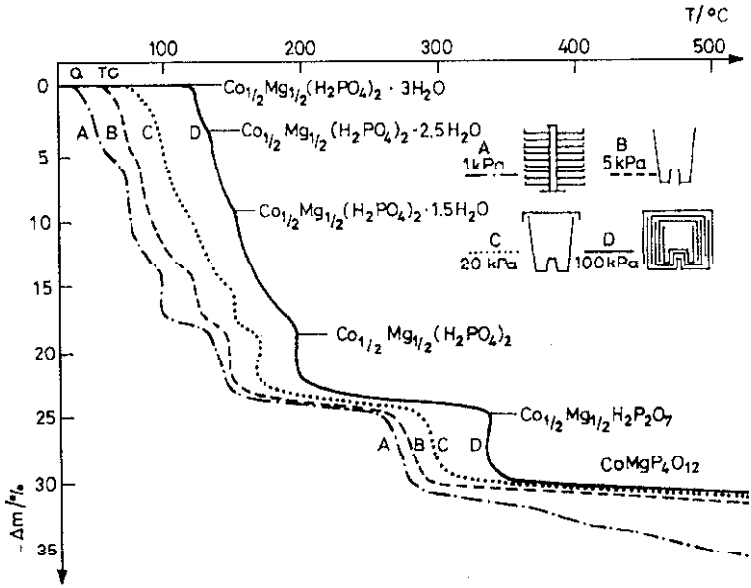

Fig. 3 Thermogravimetric curves of $Co_{0.5}Mg_{0.5}(H_2PO_4)_2 \cdot 3H_2O$ under quasi-isothermal, quasi-isobaric conditions in air. Apparatus: Derivatograph Q-1500; sample mass: 200 mg; A – multi-plate crucible, $p_{H_2O(g)}$=1 kPa; B – opened crucible, $p_{H_2O(g)}$=5 kPa; C – crucible with a lid, $p_{H_2O(g)}$=20 kPa; D – labyrinth crucible, $p_{H_2O(g)}$=100 kPa

The synthesis of the cyclo-tetraphosphates can be described by the following scheme:

$$Zn_{0.5}Mg_{0.5}(H_2PO_4)_2{\cdot}2H_2O \xrightarrow[-2H_2O]{140-185^{\circ}C} Zn_{0.5}Mg_{0.5}(H_2PO_4)_2 \xrightarrow[-H_2O]{185-230^{\circ}C} \quad (1)$$

$$Zn_{0.5}Mg_{0.5}H_2P_2O_7 \xrightarrow[-H_2O]{230-370^{\circ}C\ (350-360^{\circ}C)} 0.5c\text{-}ZnMgP_4O_{12}$$

$$Mn_{0.5}Mg_{0.5}(H_2PO_4)_2{\cdot}4H_2O \xrightarrow[-4H_2O]{120-190^{\circ}C} Mn_{0.5}Mg_{0.5}(H_2PO_4)_2 \xrightarrow[-H_2O]{190-250^{\circ}C} \quad (2)$$

$$Mn_{0.5}Mg_{0.5}H_2P_2O_7 \xrightarrow[-H_2O]{250-400^{\circ}C\ (330^{\circ}C)} 0.5c\text{-}MnMgP_4O_{12}$$

$$Co_{0.5}Mg_{0.5}(H_2PO_4)_2{\cdot}3H_2O \xrightarrow[-0.5H_2O]{120-135^{\circ}C\ (125^{\circ}C)} \quad (3)$$

$$Co_{0.5}Mg_{0.5}(H_2PO_4)_2{\cdot}2.5H_2O \xrightarrow[-H_2O]{135-150^{\circ}C\ (135-140^{\circ}C)}$$

$$Co_{0.5}Mg_{0.5}(H_2PO_4)_2{\cdot}1.5H_2O \xrightarrow[-1.5H_2O]{150-195^{\circ}C\ (150\ \ 175^{\circ}C)} Co_{0.5}Mg_{0.5}(H_2PO_4)_2$$

$$\xrightarrow[-H_2O]{200-340^{\circ}C\ (200^{\circ}C)} Co_{0.5}Mg_{0.5}(H_2P_2O_7)_2 \xrightarrow[-H_2O]{340-440^{\circ}C\ (340^{\circ}C)} 0.5c\text{-}CoMgP_4O_{12}$$

The separate reaction steps represent exothermic processes. These processes were registered by means of thermal analysis (TA) with dynamic (non-isothermal) conditions. The position of exothermic effects (axis of temperature) corresponds to temperatures mentioned in the schemes' (1), (2) and (3).

If the calcination of the starting hydrogenphosphate is performed at lower water vapour pressures, the individual intermediates (anhydride and/or dihydrogenphosphate) are partially split into hydrogenphosphates and phosphoric acid or diphosphates and diphosphoric acid, respectively. These substances can be then dehydrated and condensed separately to give side products. The amount of the main products c-$M^{II}MgP_4O_{12}$ (M^{II}=Zn, Mn, Co) in the final calcinate can be thus decreased (even below 60%, at a water vapour pressure approaching 1 kPa). At the same time, the temperatures of most of the individual dehydration reactions are also lowered.

The condensed phosphates as new colour high-temperature pigments

The methods of thermal analysis facilitate detection and explanation of processes that accompany melting of the cyclo-tetraphosphates and their recrystallization. Available papers dealing with their preparation do not give sufficiently precise data on the calcination temperatures necessary for the condensation reactions. A congruent melting of the cyclo-tetraphosphates has been presented by some authors but others presented an incongruent melting. The problem of melting is elucidated by authors of this paper. The effect of the water vapour pressure is an important factor during the condensation reactions. The presence of trace amount of water vapour decides about congruent or incongruent melting of the cyclo-tetraphosphates.

The measurements, what authors had carried out using VDTA8 M2 apparatus (system 'Kiev'), facilitated detection of the effect of the water vapour pressure on the course of the condensation reactions. This high-temperature differential

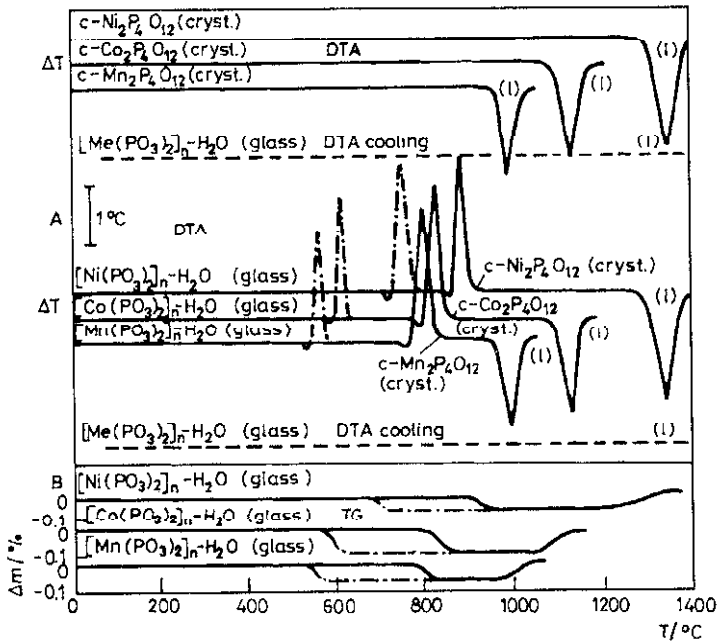

Fig. 4 (A) DTA curves of c-$Ni_2P_4O_{12}$, c-$Co_2P_4O_{12}$ and c-$Mn_2P_4O_{12}$ in a helium atmosphere (0.1 MPa) containing 2 mg H_2O per 1 He. VDTA 8 M2 apparatus (system "Kiev"); heating (cooling) rate: 40°C min^{-1}; sample mass: 100 mg; standard α-Al_2O_3; Mo crucible (opened).
(B) TG curves of $[Ni(PO_3)_2]_n \cdot H_2O$, $[Co(PO_3)_2]_n \cdot H_2O$ and $[Mn(PO_3)_2]_n \cdot H_2O$ in a wet argon atmosphere. Derivatograph, Q-1500 apparatus; heating rate: 20°C min^{-1}; sample mass: 1000 mg; standard α-Al_2O_3; Pt crucible (opened); sensitivity of the TG balance: 20 mg

thermal analyser allows measurements in vacuum or exact defined atmosphere [3]. The instruments of derivatograph [4] were used for next study of this problem (Fig. 4).

The melting of the tetrametaphosphates examined is congruent in a dry atmosphere. In the presence of small amounts of water vapour, the tetraphosphate rings are split at the melting temperature, and the chains formed are condensed to higher linear phosphates. The chains composed of several tens of $-PO_3-$ groups are ended with participation of water molecules. Reheating of the glassy products results in their crystallization with release of their water molecules and regeneration of tetrametaphosphate molecules. The reversible process can be represented (where M^{II}=Ni, Co, Mn) as follows

$$c\text{-}M_2P_4O_{12}(\text{cryst.}) \xrightarrow[\text{melting } (+4/nH_2O)]{T_{melt}} 4/nM_{n/2}H_2P_nO_{3n+1}(l) \xrightarrow[\text{solidification}]{T_{melt} \text{ to } 25^\circ C} \quad (4)$$

$$4/nM_{n/2}H_2P_nO_{3n+1}(\text{glass}) \xrightarrow[\text{softening (onset)}]{T_{soft}} 4/nM_{n/2}H_2P_nO_{3n+1}$$

$$\xrightarrow[\text{crystallization } (-4/nH_2O)]{T_{cryst}} c\text{-}M_2P_4O_{12}(\text{cryst.})$$

The detection of this reversible process was then used for the synthesis of new binary cyclo-tetraphosphates which would be found useful as new colour high-temperature pigments. The synthesis of the cyclo-tetraphosphates with combination of cations Co–Ni or Mn–Ni (scheme 5) is represented by the following scheme:

$$(1-x/2)c\text{-}Me_2P_4O_{12}(\text{cryst.}) + x/2c\text{-}Ni_2P_4O_{12}(\text{cryst.}) + 4/nH_2O \quad (5)$$

$$\xrightarrow[(\text{wet air atmosphere})]{\text{melting } [T_{melt}(Me_2P_4O_{12})=1250^\circ C]} 4/n(Me_{2-x}Ni_x)_{n/4}H_2P_nO_{3n+1}(l) \xrightarrow[(\text{solidification})]{1250^\circ C \rightarrow 25^\circ C}$$

$$4/n(Me_{2-x}Ni_x)_{n/4}H_2P_nO_{3n+1}(\text{glass}) \xrightarrow{T_{recryst}} c\text{-}Me_{2-x}Ni_xP_4O_{12}(\text{cryst.}) + 4/nH_2O$$

$$[Me - \text{Co or Mn}; T_{melt}(c\text{-}Co_2P_4O_{12}) = 1060^\circ C; T_{melt}(c\text{-}Mn_2P_4O_{12}) = 950^\circ C$$

Recrystallization of intermediates (exothermic process) and melting of the binary cyclo-tetraphosphates (endothermic process) were registered using apparatus Derivatograph 1500-D (Fig. 5).

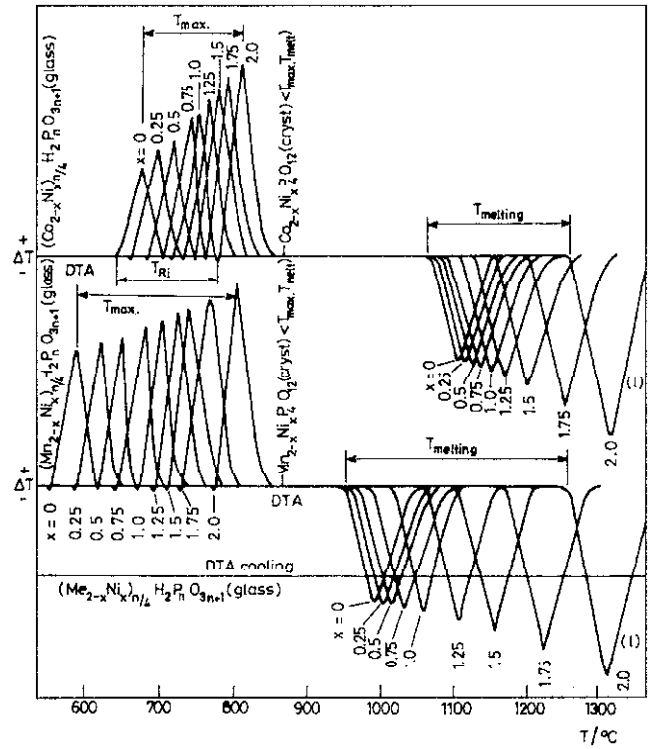

Fig. 5 The DTA curves of the vitreous intermediates $(Co_{2-x}Ni_x)_{n/4}H_2P_nO_{3n+1}$ and $(Mn_{2-x}Ni_x)_{n/4}H_2P_nO_{3n+1}$ indicating the formation of the products c-$Co_{2-x}Ni_xP_4O_{12}$ or c-$Mn_{2-x}Ni_xP_4O_{12}$ and the changes in the melting characteristics.
Sample mass: 150 mg; temperature increase: 20°C min^{-1}; Pt crucible (opened); atmosphere: air; Derivatograph, Q-1500 apparatus

Conclusions

The conditions of the synthesis of the cyclo tetraphosphates have been determined thanks to instruments of type Derivatograph that allow measurements under quasi-isothermal-isobaric conditions. New binary condensed phosphates were synthesized on the base of the results of thermal analysis. Some of these compounds are shown as new hopeful ecological anticorrosive pigments, mainly c-$Zn_{2-x}Mg_xP_4O_{12}$, c-$Zn_{2-x}Ca_xP_4O_{12}$ and c-$Mn_{2-x}Ca_xP_4O_{12}$ [5–7].

The binary products with content of cobalt [8] seem to be interesting as to their colours. These pigments are environmentally friendly and therefore very progressive, too. They belong to high-temperature pigments that are based on condensed phosphates. The synthesis of these pigments is based on the reversible process that was detected using the methods of thermal analysis.

The colour of the binary cobalt(II)-nickel(II) cyclo-tetraphosphates is an intensive blue-violet or blue-violet-brown and blue-violet-green. The colour of the binary manganese(II)-nickel(II) cyclo-tetraphosphates is an intensive yellow or yellow-green.

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