SYNTHESIS OF SPECIAL PIGMENTS
A study by means of TA methods

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Abstract

Several TA methods (including dynamic TA, Q–TA, emanation and special conductometric
TA) were used in investigations of condensed phosphate synthesis, and in the evaluation and con-
trol of the reactivity of the raw materials, when high-temperature stable pigments are developed.
Conductometric TA occupies a special position because of its high sensitivity to most changes in
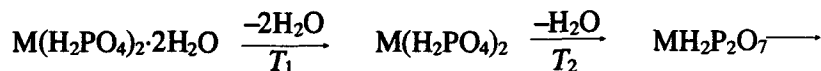crystal structure at the beginning of reactions.

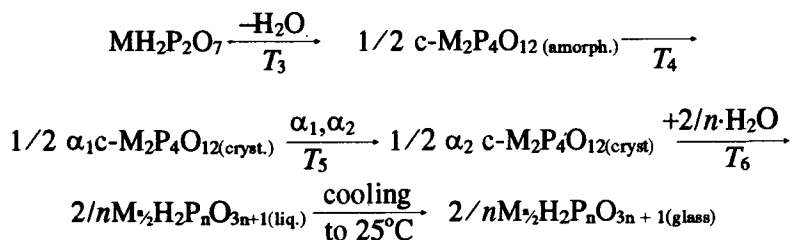Keywords: ceramics, pigments, topochemical reactions

Introduction

Our main research interest is concentrated on the synthesis of new special
pigments, e.g. those used at higher temperatures in ceramics (for ceramic
glazes, enamels or the colouring of ceramic bodies) or in paint technology as
corrosion-inhibiting materials. The syntheses of these compounds are usually
connected with high-temperature reactions in the solid state of polycrystalline
reactants. The methods of thermal analyses (TA) X-ray diffraction, SEM and
electron microprobe analysis are therefore the most useful.

For the investigation of topochemical reactions and for optimization of the
synthesis conditions, especially the following TA methods are employed: dy-
namic TA (DTA, TG), quasi-isothermal-isobaric TA (Q–TA), amperometric TA
(ATA), emanation TA (ETA), thermomechanical analysis (TMA) and differen-
tial scanning calorimetry (DSC).

The use of these methods is illustrated in some concrete cases. The scheme
of synthesis of c-tetrametaphosphates of bivalent cations (M^{2+}) can be written
as follows:

$$M(H_2PO_4)_2 \cdot 2H_2O \xrightarrow[T_1]{-2H_2O} M(H_2PO_4)_2 \xrightarrow[T_2]{-H_2O} MH_2P_2O_7 \longrightarrow$$

$$MH_2P_2O_7 \xrightarrow[T_3]{-H_2O} \quad 1/2 \ c\text{-}M_2P_4O_{12 \ (amorph.)} \xrightarrow{\quad T_4 \quad}$$

$$1/2 \ \alpha_1c\text{-}M_2P_4O_{12(cryst.)} \xrightarrow[T_5]{\alpha_1, \alpha_2} 1/2 \ \alpha_2 \ c\text{-}M_2P_4O_{12(cryst)} \xrightarrow[T_6]{+2/n \cdot H_2O}$$

$$2/nM \cdot _{1/2}H_2P_nO_{3n+1(liq.)} \xrightarrow[\text{to } 25^\circ C]{\text{cooling}} 2/nM \cdot _{1/2}H_2P_nO_{3n+1(glass)}$$

The temperatures vary with the metal cation used, e.g. for $Zn_2P_4O_{12}$ the temperatures T_1–T_6 are: 115–170°C, 170–260°C, 260–330°C, 400, 670 and 810°C.
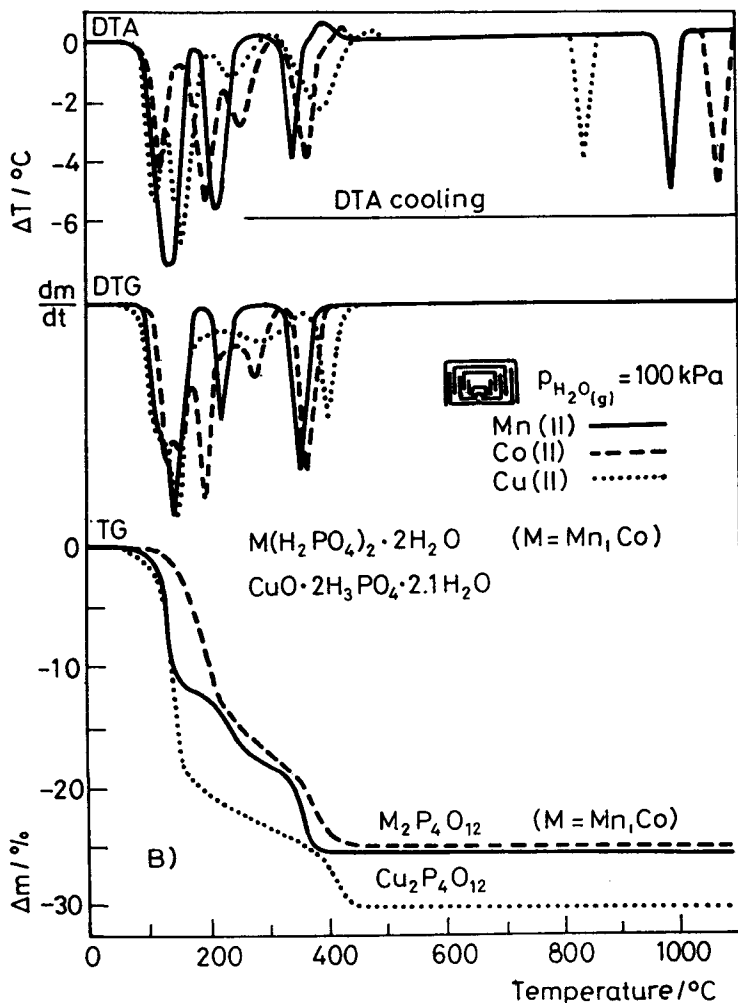

Fig. 1 Thermal curves of starting phosphates. Labyrinth crucible: $p(H_2O) = 100$ kPa; temperature increase: 2.5 deg/min in air; sample mass: 800 mg

Figure 1 illustrates the thermal decomposition of starting Mn(II) or Co(II) dihydrogenphosphate.

Cu(II) dihydrogenphosphate cannot be prepared in this way. Therefore, a mixture giving as intermediate a compound corresponding to the formula $3(CuHPO_4 \cdot H_2O) \cdot H_3PO_4 \cdot 2.5H_2O$ was used. At 150°C, the sample can be regarded as $Cu(H_2PO_4)_2$, even though it is rather a mixed product $CuHPO_4 \cdot H_3PO_4$ [1]. The release of crystal and constitutional water molecules is accompanied by a distinct endothermic effect. The small exothermic effects are connected with crystallization of the amorphous tetrametaphosphate. Another effect can be observed when various types of crucibles are used, because of the various water vapour pressures in the reaction space. This can be better demonstrated when the Q-test (Q–TA) is carried out.
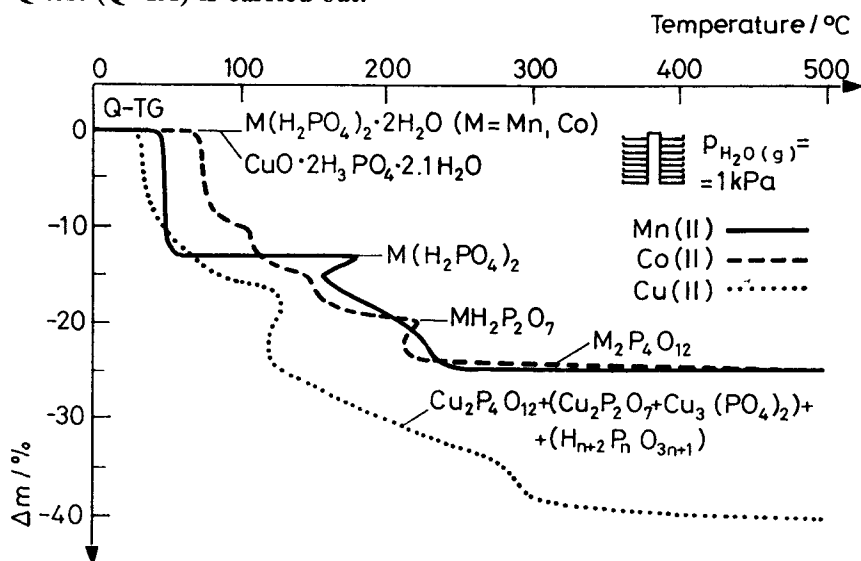

Fig. 2 TG curves of starting phosphates under quasi-isothermal, quasi-isobaric conditions. Decomposition rate: 0.4 mg·min^{-1}; polyplate crucible: $pH_2O_{(g)}$ = 1 kPa; atmosphere: air

Figures 2 and 3 show that the first step of water release for the Mn compound is sharp and isothermal. For the other compounds this is not the case. When the TG curve forms a sharp step, the reaction proceeds isothermally at the selected rate, so the reaction may be assumed to lead to equilibrium [2, 3].

If this is not so, it may be explained by presuming that the crust-like new phase formed on the surface of the starting material tends to form a compact structure. If this idea is accepted as correct, it can also be presumed that the porosity of the new phase is greatly influenced by the liberated water vapour still
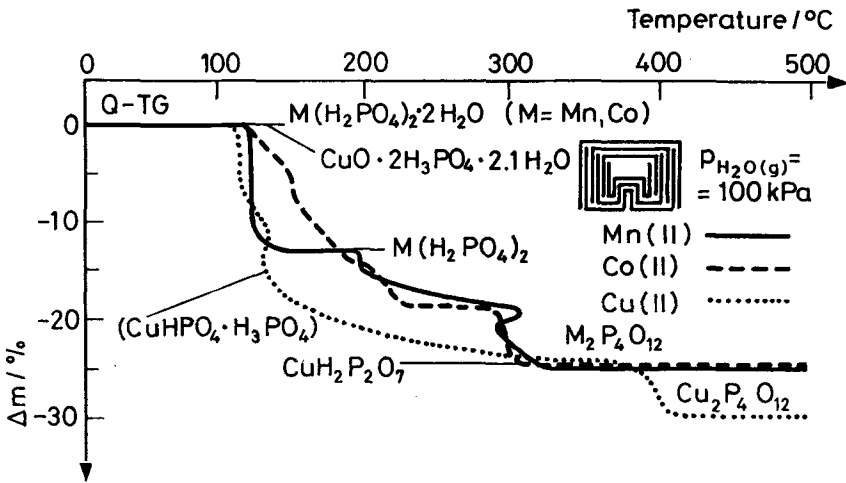
Fig. 3 TG curves of starting phosphates under quasi-isothermal conditions. Decomposition rate: 0.4 mg·min^{-1}; labyrinth crucible; $pH_2O_{(g)}$ = 100 kPa; atmosphere: air

in contact with the grains. The higher the water vapour pressure, the greater the porosity.

In this sense the difference between the curves in Fig. 4 can be interpreted [4]. In the case of curve 1 (Fig. 4), it can be assumed that in the water vapour atmosphere (100 kPa) within the labyrinth crucible, the porosity of the new phase became high enough to ensure that the water of crystallization could still depart in an isothermal way. However, in the case of curves 2, 3, 4, the reaction-retarding effect of the poor porosity prevailed.

Thus, by using these TA methods, various crucible types and measuring conditions (dynamic, Q-test) the influence of the water vapour pressure and of thermodynamic or kinetic factors may be studied. These methods allowed establishment of the conditions for producing simple or binary condensed phosphates of bi- or trivalent cations.

Another field of application of TA methods is the evaluation of the reactivity of the raw materials or reactants used to synthesize high-temperature stable ceramic pigments. When any reactant in the reaction mixture is replaced by another (the same in chemical composition and purity, but, for example, originating from another commercial production), the resulting pigment is different in hue or colour value. This effect is usually connected with the different reactivity of the new reactant. An example is the mixed spinel type pigments (e.g. $Zn/Fe_{2-x}Cr_x/O_4$, x = 1.1, a brown pigment). When different commercial products of iron oxide are used instead of the Bayferox 130 applied for this purpose by our producers, the resulting products have a different hue from that
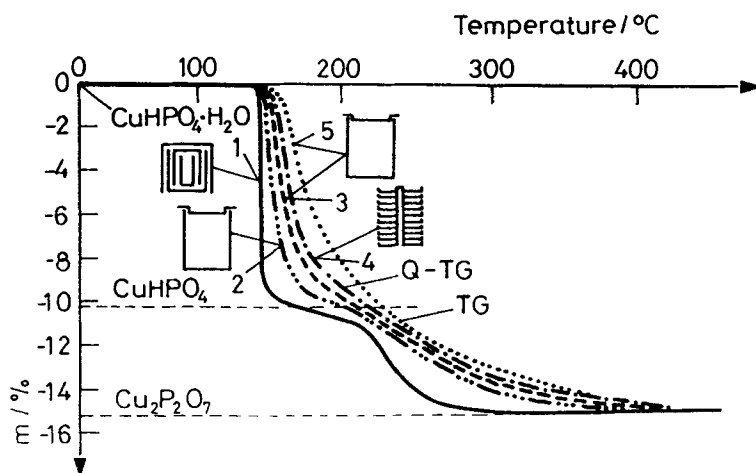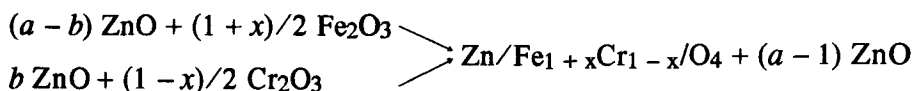
Fig. 4 Q-TG curves of hydrogenphosphate obtained in various types of platinum crucibles

brown colour. We have proved [5–7] that this can be explained by the different reactivities and kinetics of the two parallel reactions:

$$(a - b) \, ZnO + (1 + x)/2 \, Fe_2O_3 \searrow$$
$$\qquad\qquad\qquad\qquad\qquad\qquad Zn/Fe_{1 + x}Cr_{1 - x}/O_4 + (a - 1) \, ZnO$$
$$b \, ZnO + (1 - x)/2 \, Cr_2O_3 \nearrow$$

The relative reactivities of Fe_2O_3 and ZnO are shown in Fig. 5. Bayferox 130 is seen to have the lowest reactivity (the highest onset temperature of the DTA effect) of all the Fe_2O_3 samples measured. When our aim is to gain the same hue as when Bayferox 130 is used, the reactivity of another Fe_2O_3 must be decreased or that of Cr_2O_3 must to be increased. The Fe_2O_3 reactivity can be depressed by prefiring at higher temperature, but this is associated with the formation of coarser particles (the colour value then decreases). It is better to increase the reactivity of Cr_2O_3, which is possible by doping it with ions of lower valency. The most efficient appear to be Li^+ or Ni^{2+}, which can be added to the overall reaction mixture. According to the mechanism of formation of the spinel compound (Sp) (see Fig. 6), Li^+ may accelerate both reactions (Li^+ enters the octahedral positions in the spinel structure nearly as well as the tetrahedral positions, and the stabilization energy of the ligand field is small [8], whereas Ni^{2+} accelerates only the formation of $ZnCr_2O_4$, because Ni^{2+} strongly prefers octahedral positions (d^8 electron configuration, and high stabilization energy of the ligand field). Li^+ accelerates the reaction of $ZnFe_2O_4$ formation 1.2-fold, and the reaction of $ZnCr_2O_4$ 1.9–2.0-fold (at 700°C), while Ni^{2+} accelerates only the formation of $ZnCr_2O_4$ (2.2-fold). The doping of a lower valency cation in the reaction mixture causes an increase of the interstitial ions Cr_i (or Zn_i) and

therefore of the rates of diffusion and reaction too. This is especially so in the case of NiO:
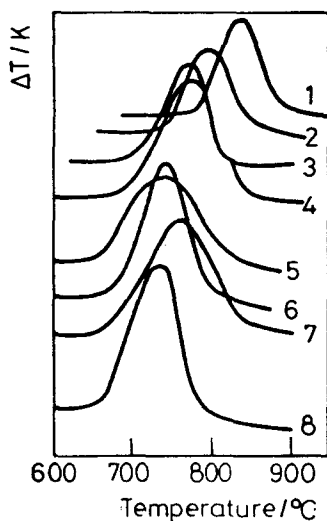
$$3NiO \longrightarrow 3Ni'_{Cr} + Cr_i^{\cdots} + Cr_2O_3$$

$$(\rightarrow ZnCr_2O_4 \text{ or } Cr_2O_3)$$

Fig. 5 DTA curves for ZnO + Fe$_2$O$_3$ (mol.ratio 1:1): rate of temperature increase: 10 deg/min; Fe$_2$O$_3$: Bayferox 130 (1), Fepren TD 202 (2), TP 303 (3), for ferrite (4), Fepren Y (5), Fepren DR (6), Fepren B (7); ZnO + Cr$_2$O$_3$ (Bayer GX) (8)

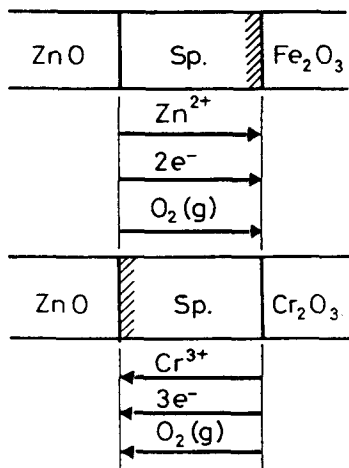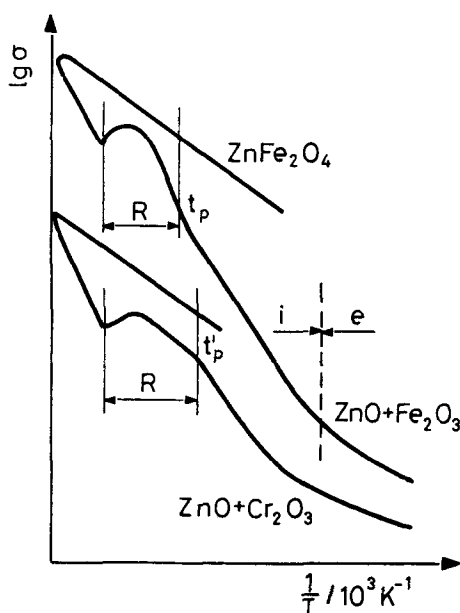Fig. 6 Mechanism of ion transport in spinel compounds

Fig. 7 ATA curves of the systems ZnO + Fe_2O_3 and ZnO + Cr_2O_3 (mole ratio 1:1) t_p, t'_p = temperature of reaction start; R = reaction zone; i, e = zone of intrinsic or extrinsic conductivity

This procedure (based on an evaluation of the reactivity) leads to a resulting brown pigment with the correct hue (the same as can be obtained with Fe_2O_3 - Bayferox 130).

The reactivities of the oxides used can be described in terms of the kinetics (k and ΔE) or the onset temperature of the DTA peak. Conductance TA (ATA [10]), indicates the temperature of the reaction start most sensitively. The ATA arrangement is detailed in [9]. The automatic LCRG-meter (TESLA BM 591) connected to a personal computer gives, for the selected temperature steps, conductivity of a sample (reaction mixture) pressed into a pastille with thin Pt plates pressed on it. Simultaneously, the temperatures are recorded. The resulting graphs of log σ vs. $1/T$ for the systems ZnO+Fe_2O_3, ZnO+Cr_2O_3 and TiO_2+Sb_2O_3 are shown in Figs 7 and 8. Measurements are carried out with alternating current with a frequency of 1000 Hz. The computer also calculates the intersection points of selected linear parts of the log σ vs. $1/T$ relationship. The points t_p (Fig. 7), the reaction start temperatures of the DTA peaks, are nearly 100 deg lower, and the differences between the various iron oxides are therefore greater. The origin of the nuclei on the grain surfaces causes a change in the conductivity, which is sensitively detected by the described device.
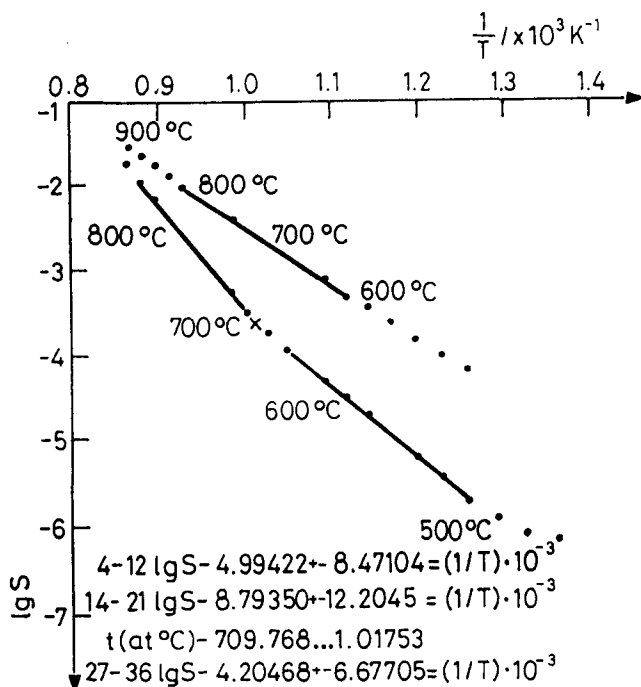
Fig. 8 Conductance curve of solution of Sb_2O_3 (5%)-TiO_2 (Pretiox AV-01). The point of intersection indicates the start of solution and rutile formation ($t=709.77°C=710°C$). Rate of increase of temperature 5 deg/min

Figure 8 illustrates the use of the ATA method to determine the temperature of entry of Sb_2O_3 into TiO_2. The structure of TiO_2 changes from the anatase to the rutile form. At 780°C, the reaction mixture exhibited small diffraction patterns of the rutile structure when RTG analysis was carried out on the cooled sample. At 840°C, the rutile content was about 25–35%. When pure anatase is measured, the relationship log σ vs. $1/T$ shows an intersection about 100 deg higher (at 798°C).

This method has been employed for estimation of the reactivities of various TiO_2 and ZrO_2 oxides for investigation of the synthesis of rutile and zircon-type pigments.

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Zusammenfassung — Verschiedene thermoanalytische Methoden (DTA, Q-TA, Emanations- und spezielle konduktometrische TA) wurden in Untersuchungen kondensierter Phosphatsynthe- se und in der Auswertung und Kontrolle der Reaktivität von Rohstoffen bei der Entwicklung von hochtemperaturbeständigen Pigmenten angewendet. Dabei nimmt die konduktometrische TA we- gen ihrer hohen Empfindlichkeit gegenüber den meisten Veränderungen in der Kristallstruktur bei Reaktionsbeginn eine Sonderstellung ein.