Obtaining and Characterization of New Ceramic Pigments for Polychrome Artistic Elements

III. Thermogravimetric analysis

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The paper presents the thermal characterisation of 18 photostable pigments obtained by co-precipitation in aqueous systems, based on precursors with chromophore structures of zinc phosphate and chromate, chemically doped with Mn(II), Fe(II), Fe(III), Co(II), Ni(II) and Bi(III) cations. The thermal analysis of the precursors highlighted the thermal stability of the pigments and the mass losses, as well as the phase changes that occurred within the 25 - 900°C temperature range. Based on the acquired data the 18 pigments were grouped, according to their thermal stability, into four possible domains of application: obtaining glazed polychrome elements and water and oil based paints. Even if they were obtained from the same precursors, namely zinc phosphate and chromate, as basic materials for synthesizing ceramic pigments by doping with chromophore cations, after co-precipitation in aqueous systems the obtained pigments had different thermal behaviour. Thus, the first group contains pigments with high chemical and thermal stability, namely P.1, P.2, P.3, P.4, P.7, P.8, P.10 and P.12, that are suitable in fritted applications for polychrome tiles for mosaics and stained glasses. The second group, that of the less stable pigments, can be used for oil or water based painting, includes: P.5, P.6, P.8, P.10, P.11, P.12, P.13, P.14, P.15 and P.16.

Keywords: Ceramic pigments; Chromophore elements, TG, DTA, DTG, Thermal stability

Relevant publications in the field contain several examples of thermal analysis methods in dynamic behaviour used in the study of ceramic pigments stability alteration. The focus is usually on the influence of the chemical or physical doping of the chromophore precursors with various cations from the p, d or f metal block on their chemical or physical behaviour used in the study of ceramic pigments stability. Thus, the first group contains pigments with high chemical and thermal stability. Based on the acquired data the 18 pigments were grouped, according to their thermal stability, into possible domains of application: obtaining glazed polychrome elements and water and oil based paints. Even if they were obtained from the same precursors, namely zinc phosphate and chromate, as basic materials for synthesizing ceramic pigments by doping with chromophore cations, after co-precipitation in aqueous systems the obtained pigments had different thermal behaviour. Thus, the first group contains pigments with high chemical and thermal stability, namely P.1, P.2, P.3, P.4, P.7, P.8, P.10 and P.12, that are suitable in fritted applications for polychrome tiles for mosaics and stained glasses. The second group, that of the less stable pigments, can be used for oil or water based painting, includes: P.5, P.6, P.8, P.10, P.11, P.12, P.13, P.14, P.15 and P.16.

Keywords: Ceramic pigments; Chromophore elements, TG, DTA, DTG, Thermal stability

of simple and binary compounds, that actually start at temperatures lower than 400°C occurs.

For the same precursor, Antraptseva et al. [4] detected from the TG curve data the water content chemically bound of 20.02% for Ca(H₂PO₄)₂ (very close to the theoretical values of 21.42%), 25.27% for Mn(H₂PO₄)₂ and 20.81% for Ca,Mn₃(H₂PO₄)₂·H₂O, as found by other published studies on hydrated binary metallic hydrogen phosphates in the field [5-7].

The binary calcium and manganese cyclo-tetraphosphate, CaMnP₂O₉, is known as the final product of the thermal breakdown of Ca,Mn₃(H₂PO₄)₂·H₂O at temperatures of over 400°C. The thermal behaviour of the burnt compound, CaMnP₂O₉, and of those individually hydrated, Mn(H₂PO₄)₂·2H₂O and Ca(H₂PO₄)₂·2H₂O, confirm the appearance of the binary compound with the Ca₉,Mn₃(H₂PO₄)₂·H₂O formula. Moreover, according to [8], that newly synthesized compound, Ca₉,Mn₃(H₂PO₄)₂·H₂O, has a different thermal behaviour than that found in [4], possibly due to the different water content and preparation methods.

The TG-DTG-DTA curves of the Mn₈,Cu₈(H₂PO₄)₂·1.5H₂O precursor have two temperature intervals, namely 97-150°C and 150-300°C, where mass loss of 9.19% and
10.83% occurs, corresponding to 1.48 and 1.74 water moles. The thermal breakdown of Mn$_2$Cu$_4$ (H$_2$PO$_4$)$_4$.1.5H$_2$O is a complex process that involves, firstly, crystallisation water loss (1.5 mole) and secondly of the two water molecules chemically bound, present in the intermolecular structures of the hydro-phosphate groups. Resulting from those breakdown processes up to 350°C is the MnCuP$_2$O$_7$, binary manganese copper cyclo-tetraphosphate. The thermal behaviour is affected by the insertion of the Cu(II) cation in the initial MnHPO$_4$.1H$_2$O structure [9].

The TG curve of the MnHPO$_4$.1H$_2$O precursor indicates a series of mass losses between 30 and 800°C, due to the elimination of the three water types (hygroscopic, crystallisation and chemically bound) from the hydro-phosphate structures. The elimination of the chemically bound water leads to the appearance of piro-bonds, with phase transformation. Thus, two temperature ranges for water elimination are noticed: the first one at 130-320°C for hygroscopic and crystallisation water, and 320-420°C for chemically bound water, with losses of 10.11% (0.94 water moles) and of 6.89% (0.64 water moles) of the initial mass. The exothermic effect at 571°C seen on the DTA curve, which does not have a significant mass decrease, is caused by a transformation in the transition phase, the change from the amorphous state to the crystalline one of Mn$_2$P$_2$O$_7$.

The crystallisation water, considered anionic water, cannot be usually removed without destroying the anion structure, which confirms the fact that the two water elimination processes (crystallisation and chemically bound water) are often overlapped on a certain temperature range. At temperatures above 420°C the Mn$_2$P$_2$O$_7$ manganese pyrophosphate is the final product of the thermal breakdown of the precursor and the total mass loss is 17.00% (1.58 H$_2$O moles), very close to the theoretical one of 16.17%, which corresponds to 1.50 H$_2$O moles [10].

Similar thermal processes, of losing the three water types, occur in the Co(H$_2$PO$_4$)$_2$.2H$_2$O type precursors, that change, up to 600°C, into the Co$_2$P$_4$O$_{12}$ cobalt cyclo-tetraphosphate [11-12].

The thermal analysis for Zn(II), Bi(III) and/or Sb(III) oxohydroxides based pigments highlights the fact that the co-precipitation process in an ammonia system allows the accomplishment of phase redistribution at more elevated temperatures than the procedure of precipitation in a strong alkaline environment, when a series of congruents, that reform structurally at lower temperatures, is obtained, thus creating the best conditions for the eutectoid of antimony and the bismuth oxides, as dispersion environment for spinel grains [13-15].

The DTA analysis of the precursors obtained by co-precipitation is in compliance with that of the ones obtained by other means and indicates the appearance of new chemical compounds that differ from the specific compounds (individual hydroxides). The pigments obtained by the co-precipitation of oxohydroxides show big thermal losses for hygroscopic and chemically bound water, as confirmed by the DTA and TG curves [16,17].

In the present study, the newly synthesized pigments, previously analysed by SEM-EDX and FTIR [18] and also by CIEL*a*b* colorimetric and optical microscopy [19] were analysed by thermogravimetry, in order to select two pigment groups, for fitted systems and for water and oil colours, based on their thermal and chemical stability.

**Experiment part**

**Materials and methods**

Thermogravimetric determinations for the 18 pigment samples, obtained by co-precipitation in aqueous systems were done with a STA Perkin-Elmer derivatograph and, according to the chromophore cations used in synthesis, they were divided into 7 classes, as follows:

- **Group I**, that contains only the cation Zn(II) and is formed of two pigments indexed as: P1 (synthesized in a mild acid medium, at pH = 6.5, with the chromophore anion: PO$_4^{3-}$) and P2 (synthesized in an alkaline medium, at pH = 10.5, with the chromophore anions: CrO$_4^{2-}$ and PO$_4^{3-}$). The two pigments were considered as reference points for the present study.

- **Group II**, that contains the cation Zn(II) and Mn(II), consisting of three pigments indexed as: P3 (synthesized in an alkaline medium, at pH = 9.5, with the chromophore anions: CrO$_4^{2-}$ and PO$_4^{3-}$) and P4 and P5 (the first one synthesized in a mild acid medium, at pH = 6.5 and 7.5 for the second, with the chromophore anions: Cr$_2$O$_7^{2-}$ and PO$_4^{3-}$);

- **Group III**, that contains the cation Zn(II) and Fe(II), formed of three pigments indexed as: P6 and P7 (the first synthesized in an alkaline medium, at pH = 8.0, the second at pH = 9.5 with the chromophore anions: CrO$_4^{2-}$ and PO$_4^{3-}$) and P8 (synthesized in a neutral medium, at pH = 7.0, with the chromophore anion: PO$_4^{3-}$);

- **Group IV**, that contains the cation Zn(II) and Fe(III), formed of other three pigments indexed as: P9 and P10 (synthesized in an alkaline medium, at pH = 8.5, the second at pH = 9.5 with the chromophore anions: CrO$_4^{2-}$ and PO$_4^{3-}$) and P11 (in a mild alkaline medium at pH = 6.5, with the chromophore anion: PO$_4^{3-}$);

- **Group V**, that contains only the cation Zn(II) and Co(II) and is formed of two pigments indexed as: P12 and P13 (the first synthesized in a neutral medium, at pH = 7.0, with the chromophore anion: PO$_4^{3-}$ and the second, synthesized in an alkaline medium, at pH = 9.5, with the chromophore anions: CrO$_2^{2-}$ and PO$_4^{3-}$);

- **Group VI**, that contains only the cation Zn(II) and Ni(II), is formed of four pigments indexed as: P14 and P15 (the first synthesized in an alkaline medium, at pH = 8.5, the second, without the Zn (II) cation, only with Ni (II), at pH = 9.5 with the chromophore anions: CrO$_2^{2-}$ and PO$_4^{3-}$) and P16 and P17 (the first one synthesized in a neutral medium, at pH = 7.0 and 6.5 for the second, with the chromophore anion: PO$_4^{3-}$);

- **Group VII**, formed only of pigment P18, which contains the cations Zn(II) and Bi(II), synthesized in a mild acid medium, at pH = 6.5, with the chromophore anions: Cr$_2$O$_7^{2-}$ and PO$_4^{3-}$).

In the thermogravimetric analysis 50 mg of each product, which was firstly finely ground then dried in a drying chamber at 110±5°C for four hours, was taken. The thermal analysis was done in dynamic conditions, with a heating rate of 10°C/min between 25 and 950°C.

During the processing of analytical data a series of characteristics from the pigments derivatograms were taken into consideration, namely: TG$_{expt}$ – the temperature where the thermal degradation in each stage begins; TG$_{in}$ – the temperature where the thermal degradation ends; DTA – temperature corresponding to DTA peaks, and W$_{tota}$ - total mass loss at final temperature of 950°C.

For a complete characterisation of the newly synthesized pigments their thermal stability was observed for different ranges of significant temperatures, with specific processes of thermal degradation.
Results and discussions

The two pigments from group I, labelled P.1 and P.2, have Zn(II) as chromophore cation and the precursor anion for P.1 is phosphate and for P.2 phosphate and chromate. Their thermal behaviour was taken as reference for comparison.

In figure 1 the TG and DTA curves of P.1 and P.2 are presented and in table 1 their thermogravimetric data.

Between 30 and 160°C the P.1 pigment has a thermal process with a dominant endothermic effect, with a peak at 117°C, due to the loss of hygroscopic water and the absorption of oxygen from the air flow; in this temperature range the mass loss is significant of 6.5%. Between 160 and 180°C, a weak endothermic process is noticed, because of structural permutations and of the loss of partially reversible hygroscopic water and of adhesion water, with a mass loss of 1.0%. Two endothermic actions follow between 180 and 386°C with peaks at 212 and 265°C, when the structures are transformed by losing water from hydro-gels and hydro complexes; in this range the mass loss is of 14.3%. This is followed by a slightly exothermic process between 386 and 500°C, due to pre-sintering actions, with mass loss of 2.0%. At the end two consecutive exothermic processes take place, the first one between 231 and 373°C, due to structural permutations by losing partially reversible hygroscopic water, when the mass drop is of 3.5%, the second between 385 and 425°C which is a physical phenomena with no mass loss and the last between 425 and 565°C, with peaks at 490 and 516°C when the structures are transformed by losing water from hydro-gels and hydro complexes; in this temperature range the mass loss is of 1.4%. At the end there is an endothermic process in two stages, between 752 and 842°C, with peaks at 807°C and 829°C and there is no mass loss in this range.

The P.3, P.4 and P.5 pigments from group II, have Mn(II) as chromophore cation, besides Zn(II) from the precursor. Figure 2 shows the derivatograms of the P.3, P.4 and P.5 pigments.

Table 2 shows thermalgravimetric data for the P.3, P.4 and P.5 pigments.

Processes follow between 444 and 695°C with peaks at 481, 595 and 656°C when the structures are transformed by losing water from hydro-gels and hydro complexes but without significant effect on the rate of mass loss. From the DTA curve three thermal processes with significant peaks can be noticed: the first one, exothermic, between 223 and 265°C, with a peak at 246°C, the second one, exothermic too, between 404 and 415°C with a peak at 409°C and the third one, endothermic, between 727 and 788°C with a peak at 774°C, all with no mass loss. The global mass loss at 950°C was of 30.0%.

The P.3, P.4 and P.5 pigments from group II, have Mn(II) as chromophore cation, besides Zn(II) from the precursor. Figure 2 shows the derivatograms of the P.3, P.4 and P.5 pigments.

Table 2 shows thermalgravimetric data for the P.3, P.4 and P.5 pigments.

The P.3 pigment has, between 30 and 231°C, a thermal process with a dominant endothermic effect, with a peak at 129°C, due to the loss of reversible hygroscopic water and the absorption of an oxygen quantity from the atmosphere; in this range the mass loss is of 14.3%. This is followed by a slightly exothermic process between 231 and 373°C, due to pre-sintering actions, with mass loss of 2.0%. At the end two consecutive exothermic processes take place, the first one between 231 and 373°C, due to structural permutations by losing partially reversible hygroscopic water, when the mass drop is of 3.5%, the second between 385 and 425°C which is a physical phenomena with no mass loss and the last between 425 and 565°C, with peaks at 490 and 516°C when the structures are transformed by losing water from hydro-gels and hydro complexes; in this temperature range the mass loss is of 1.4%.

At the end there is an endothermic process in two stages, between 752 and 842°C, with peaks at 807°C and 829°C and there is no mass loss in this range.

The P.4 pigment has a thermal process between 30 and 180°C, with a dominant endothermic effect and a peak at...
101°C, due to the loss of reversible hygroscopic water and the absorption of an oxygen quantity from the atmosphere; in this range the mass loss is of 12.8%. Then an exothermic process follows between 200 and 256°C with peak at 233°C, due to structural permutations by losing partially reversible hygroscopic water. In this range the mass loss is of 2.6%. There follows another exothermic process, between 202 and 452°C, with a peak at 422°C when the structures are transformed by losing water from hydro-gels and hydro complexes. In this range the mass loss is of 2.1% and in the end there is an endothermic process in two stages between 422 and 641°C with peaks at 488 and 612°C due to pre-sintering processes, with a mass loss of 2.8%.

The P5 pigment has, between 36 and 245°C, a thermal process with a dominant endothermic effect, with a peak at 116°C, due to the loss of reversible hygroscopic water and the absorption of a certain oxygen quantity from the atmosphere. In this range the mass loss is of 12.1%. Then there is a mild endothermic one between 245 and 307°C, with a peak at 267°C due to structural permutation by losing partially reversible hygroscopic water. In this range the mass loss is insignificant (1.0%). An endothermic process follows between 307 and 362°C with a peak at 330°C when the structures are transformed by loss of water from hydro-gels and hydro-complexes, with insignificant mass loss in this range (1.0%). At the end a mild endothermic process occurs between 448 and 736°C due to pre-sintering reactions and in which the mass loss is very low (2.3%).

The P6, P7 and P8 pigments, from group III, have Fe(II) as chromophore cation besides Zn(II) from the precursor. In figure 3 the derivatograms of P6, P7 and P8 pigments are presented.

Table 3 presents the thermogravimetric data of the P6, P7 and P8 pigments.

The P6 pigment has between 43 and 225°C, a thermal process with a dominant endothermic effect, with a peak at 142°C due to the loss of reversible hygroscopic water and the absorption of an oxygen quantity from the atmosphere; in this range the mass loss is of 13.8%. A mild exothermic process occurs between 253 and 360°C due to structural permutation by loss of partially reversible hygroscopic water, the mass loss in this temperature range being low (2.8%). At the end there is an exothermic process between 407 and 527°C, with a peak at 484°C, when the structures are transformed by losing inherent water from hydro-gels and hydro complexes. There is an insignificant mass loss of 1.0% in this range.

The P7 pigment has between 39 and 172°C a thermal process with a dominant exothermic effect with a peak at 122°C due to the loss of reversible hygroscopic water and the absorption of an oxygen quantity from the atmosphere. In this range the mass loss is of 9.20%. There follows an endothermic one between 172 and 233°C, due to structural permutation by loss of partially reversible hygroscopic water, the mass loss in this temperature range being of 4.5%. An exothermic process follows between 247 and
309°C, with peak at 484°C, when the structures are transformed by losing inherent water from hydro-gels and hydro complexes with a mass loss of 2.8%. Then an endothermic process follows between 497 and 584°C, with peak at 563°C due to pre-sintering reactions where the mass loss is of 1.1%. At the end an endothermic process occurs between 650 and 728°C, with a peak at 706°C, with an insignificant mass loss of 0.4%.

The P.9 pigment has between 43 and 198°C a thermal process with a dominant endothermic effect, with a peak at 136°C due to the loss of reversible hygroscopic water and the absorption of an oxygen quantity from the atmosphere. In this range the mass loss is of 14.5%. Then it follows an exothermic one in two stages, between 198 and 289°C, with peaks at 236 and 258°C, due to structural permutations by loss of partially reversible hygroscopic water, with a 5.9% mass loss. An endothermic process follows between 333 and 374°C, with a peak at 354°C, when part of the crystallisation and coordinative water is eliminated and the mass loss is of 2.1%, followed by an exothermic one, between 374 and 486°C, with a peak at 429°C when structures are transformed by loss of the inherent water from the hydro-gel and hydro complexes with a 3.50% mass loss in this range. Two sigmoid endothermic processes follow, the first one, mild endothermic, between 695 and 742°C, and the second one, a strong one, between 742 and 780°C, with peak at 763°C, due to pre-sintering reactions where the mass loss is of 0.4%, for the first zone and of 0.2% for the second one. At the end there are two endothermic processes: the first between 861 and 908°C with a peak at 890°C and small mass loss of 0.4% and the second one between 908 and 934°C with an insignificant mass loss.

The P.9, P.10 and P.11 pigments from group IV also have Fe(II) as chromophore action besides Zn(II) from the precursor.

In figure 4 the derivatograms of the P.9, P.10 and P.11 pigments are shown.

Table 4 presents the thermogravimetric data of the P.9, P.10 and P.11 pigments.
between 236 and 292°C with a peak at 250°C due to structural permutations by loss of partially reversible hygroscopic water, with a 2.7% mass loss, then another endothermic one between 300 and 335°C, when the mass loss is of 1.4%, this one being followed by an exothermic one between 392 and 477°C, with a peak at 440°C when structures are transformed by loss of inherent water from hydro-gels and hydro complexes, with a 1.9% mass loss. There is an endothermic process in two steps, one between 493 and 610°C when another one between 546 and 586°C overlaps, with a peak at 568°C due to pre-sintering reactions and with mass loss of 1.7%, followed by two exothermic physical processes, one between 632 and 677°C, with a peak at 653°C and the other one between 753 and 794°C, with a peak at 774°C; these take place with no mass loss. In the end there are three strongly endothermic sigmoid processes: the first one between 823 and 860°C, with a peak at 846°C, the second one very strong, between 860 and 904°C and a peak at 890°C and the third one between 904 and 925°C with a peak at 915°C and no mass losses.

The P10 pigment has between 40 and 206°C a thermal process with dominant endothermic effect, with a peak at 149°C, due to loss of hygroscopic water and absorption of an oxygen quantity from atmosphere, with a 9.4% mass loss in this range. Then there is an exothermic one between 206 and 254°C, with a peak at 233°C due to structural permutations by loss of the partially reversible hygroscopic water, with a mass loss of 1.6%. Another endothermic process follows between 285 and 336°C, with a peak at 307°C, when structures are transformed by the loss of the inherent water from hydro-gels and hydro complexes. In this range the mass loss is of 1.7%. It is followed by an exothermic process, between 345 and 398°C, with a peak at 364°C, when part of the crystallisation and coordinative
water is eliminated and the mass loss is of 1.1%. Then there is a mild endothermic process in two steps, between 398 and 580°C, with peaks at 460 and 543°C, due to pre-sintering reactions, where the mass loss is of 2.0%. At the end three processes of which the first two exothermic, one between 617 and 667°C with a peak at 650°C and one between 693 and 753°C. The third one is endothermic, between 875 and 914°C, with a peak at 902°C, with no mass loss.

The \( P.11 \) pigment has between 35 and 258°C a thermal process with a dominant endothermic effect, with a peak at 154°C, due to the loss of hygroscopic water and the absorption of an oxygen quantity from the atmosphere with mass loss in this range of 18.6%. This is followed by another endothermic one between 305 and 334°C with peak at 324°C due to structural permutations, with a mass loss in this range of 4.5%. Then it follows an exothermic process, between 427 and 472°C, with a peak at 450°C, when structures are transformed by the loss of inherent water from hydro-gels and hydro complexes, with a mass loss in this range of 0.8%. An endothermic process follows between 490 and 574°C with a peak at 513°C, with an overlapped endothermic process between 513 and 574°C with a peak at 541°C, due to pre-sintering reactions; the mass loss is of 1.6%. In the end there is an endothermic process, between 863 and 941°C, with a peak at 933°C, when the mass loss is very low, of 0.6%.

The \( P.12 \) and \( P.13 \) pigments from group V have Co(II) as chromophore cation, besides Zn(II) from the precursor.

Figure 9 contains the derivatograms of the \( P.12 \) and \( P.13 \) pigments.

Table 5 contains the thermogravimetric data of the \( P.12 \) and \( P.13 \) pigments.

The \( P.14 \), \( P.15 \), \( P.16 \) and \( P.17 \) pigments from group VI have Ni(II) as cation chromophore, besides Zn(II) from the precursor.

Figure 6 presents the derivatograms of the \( P.14 \), \( P.15 \), \( P.16 \) and \( P.17 \) pigments.

Table 6 contains the thermogravimetric data for the \( P.14 \), \( P.15 \), \( P.16 \) and \( P.17 \) pigments.
The **P14** pigment has between 27 and 228°C a thermal process with a dominant endothermic effect in two overlapping steps: the first one at 149°C, that has a more pronounced endothermic effect, and the second one with a peak at 168°C that has a faster rate, corresponding to the elimination of reversible hygroscopic water and the absorption of a certain oxygen quantity from the atmosphere, with a mass loss in this range of 6.0%. Then there is an endothermic one between 228 and 275°C with a peak at 252°C, due to the loss of partially reversible hygroscopic water and structural permutations, with a mass loss in this range of 0.9%. It is followed by an endothermic process between 286 and 356°C with a peak at 320, when structures are transformed by the loss of inherent water from hydro-gels and hydro complexes with mass loss in this range of 1.5%. An endothermic process follows between 390 and 457°C with a peak at 435°C, due to pre-sintering reactions, when the mass loss is of 1.7%. This process is followed by an exothermic one between 480 and 507°C, with no significant effect on the mass loss; then an endothermic one occurs between 507 and 598°C with peak at 553°C when mass loss is of 3.0%. At the end and endothermic process occurs between 677 and 730°C with a peak at 700°C and no mass loss.

The **P15** pigment has between 25 and 227°C a thermal process with a dominant endothermic effect in two overlapping stages: the first one at 145°C, that has a more pronounced endothermic effect, and the second one with a peak at 168°C that has a faster rate, corresponding to the elimination of reversible hygroscopic water and the absorption of a certain oxygen quantity from the atmosphere, with a mass loss in this range of 6.2%, then an endothermic one occurs between 273 and 345°C with peak at 316°C, due to the loss of partially reversible hygroscopic water and structural permutations with a mass loss of 2.6%.
in this range. An endothermic process follows between 396 and 453°C, with a peak at 431°C, when structures are transformed by loss of inherent water hydro-gels and hydro complexes and the mass loss in this range is 2.2%. Then there is another endothermic one between 497 and 537°C with a peak at 500°C, due to pre-sintering reactions, when the mass loss if of 3.0% and at the end there is an endothermic one between 679 and 717°C, with a peak at 701°C and no mass loss.

The pigment has between 24 and 238°C a thermal process with a dominant endothermic effect with two overlapped stages, with peak at 103°C, due to loss of reversible hygroscopic water and oxygen absorption from the atmosphere, with a mass loss in this range of 18.5%. Then two successive endothermic ones follow in the 238-317-346°C range, with peaks at 282°C and 329°C; the first one with a more pronounced thermal effect due to the loss of partially reversible hygroscopic water and structural permutations, with a mass loss of 5.40%, then an endothermic one follows between 346 and 454°C with a peak at 395°C, when structures are transformed by the loss of inherent water from hydro-gels and hydro complexes and the mass loss in this range is 3.3%. An exothermic process follows between 499 and 559°C with a peak at 528°C, due to pre-sintering reactions and the mass loss is of 3.0%. There follows an endothermic process between 640 and 698°C with a peak at 664°C, when the mass loss is of 0.8%, and at the end there is an endothermic one between 826 and 898°C, with a peak at 844°C, and no significant variation of mass loss.

The pigment has between 24 and 238°C a thermal process with a dominant endothermic effect with two overlapped stages, with peak at 103°C, due to loss of reversible hygroscopic water and oxygen absorption from the atmosphere, with a mass loss in this range of 18.5%. Then two successive endothermic ones follow in the 238-317-346°C range, with peaks at 282°C and 329°C; the first one with a more pronounced thermal effect due to the loss of partially reversible hygroscopic water and structural permutations, with a mass loss of 5.40%, then an endothermic one follows between 346 and 454°C with a peak at 395°C, when structures are transformed by the loss of inherent water from hydro-gels and hydro complexes and the mass loss in this range is 3.3%. An exothermic process follows between 499 and 559°C with a peak at 528°C, due to pre-sintering reactions and the mass loss is of 3.0%. There follows an endothermic process between 640 and 698°C with a peak at 664°C, when the mass loss is of 0.8%, and at the end there is an endothermic one between 826 and 898°C, with a peak at 844°C, and no significant variation of mass loss.

Conclusions
The dynamic thermal analysis of the 18 newly synthesized pigments highlights the fact that co-precipitation in an alkaline environment allows phase redistribution to be accomplished at higher temperatures than in neutral or mild acid ones.

According to the TG curves P1 is more thermally stable than P2, P4 is more thermally stable than P3 and P5, P7 more than P6 and P8. P6 and P8 have an almost equal thermal stability; P9, P10 and P11 have an almost equal thermal stability and P9 and P10 have a better thermal stability than P11; P12 and P13 have almost the same thermal stability; P17 is more thermally stable than P15, P16 and P14 (P14 has the lowest thermal stability of all three pigments); P18 is thermally stable from 600°C.

According to the observations above and in correlation with other already published results [9,10], out of the 18 newly synthesized pigments for polychrome glazed artistic elements (mosaic, stained glass, coloured pottery, etc.) only P1, P4, P7, P9, P10, P17 and P18 can be successfully
used. The rest, P2, P3, P5, P6, P8, P11, P12, P13, P14, P15 and P16, can be used for sicative oil or water based paints.

References
11. LAZĂU, I., BORCĂNESCU(JANOȘEV), S., PĂCURARIU, C., LAZĂU, R., COROVIȚĂ, I., Revista Română de Materiale, 40, 2010, p.28-40
16. PISHCH, I.V., RADION, E.V., Glass and Ceramics, 62, 2005, p. 189

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