

Obtaining and Characterization of Ceramic Pigments for Polychrome Artistic Elements

I. Synthesis and SEM-EDX and μ -FTIR Analysis

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The present paper presents the synthesis and chemical characterization of 18 thermally and photo-resistant ceramic pigments, obtained by aqueous system coprecipitation, based on a zinc phosphate and chromate/dichromate chromophore structure (considered as basic precursor), chemically doped with Mn(II), Fe(II), Fe(III), Co(II), Ni(II) and Bi(III) cations. The pigments are intended for painting purposes or as fritted pigments for mosaics or stained glass. Following the synthesis in an alkaline, neutral, or mild acid aqueous medium (according to case), the precipitates were washed, dried and calcinated, then analyzed by SEM-EDX and micro-FTIR. The results obtained revealed the chromophore species involved in precipitation, by correlation of the molar ratios used in the synthesis and the elemental chemical composition identified by EDX. The SEM micro-photographs revealed the morphology and the granulometry of the powder and the micro-FTIR confirmed the composition of the newly synthesized pigment.

Keywords: ceramic pigment, SEM-EDX, micro-FTIR, coprecipitation, synthesis, polychrome layer

Relevant publications in the field [1, 2] present blue-violet ceramic pigments, synthesized by coprecipitation to a solid phosphate solution of Fe(III) and Co(II), through processes of slow interdiffusion in a solid state. The morphology, homogeneity and the composition of those pigments were analyzed by SEM-EDX, and were attributed the formula $\text{Co}_{2-x}\text{Mg}_x\text{P}_2\text{O}_7$, where x varies between 0.5 and 1.5.

The pink pigments with the $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ stoichiometries can only be obtained if the Al_2O_3 content is higher than the Cr_2O_3 content. For that purpose a composition with a low chrome concentration was developed. A pigment with the $\text{Al}_{1.55}\text{Cr}_{0.45}\text{O}_3$ (78% mol Al_2O_3 - 22% mol Cr_2O_3) stoichiometry corresponds to the limit between the green and red color gradients [3].

The ceramic pigment with the $\text{Zn}(\text{AlCr})_2\text{O}_4$ formula corresponds to a pink color pigment that was traditionally synthesized in solid state, based on an interdiffusion reaction between the reagents. The high reaction temperatures involved in those processes require the use of certain additives (easily fuzable ones), in order to decrease the thermal threshold that allows interdiffusion. To decrease the synthesis temperature one can calcinate the finely dispersed amorphous precipitate. Thereby, the pigment synthesis temperature can be reduced by 150-200°C and the energy consumption is 10-20% lower, yet the quality parameters of the chromophore are kept intact. The chromatic characteristics of the pigment depend on the crystal domain around the chromophore ion. Thus, another way to obtain various red pigments is to intensify the crystal field around the Cr^{3+} ion [4].

Moreover, there are inorganic pigments from the M(I) and M(II) dihydrogenophosphates class that were synthesized from the carbonates of their corresponding metals in reaction with orthophosphoric acid at low temperatures (40-80°C), which can last from 2 to 60 h. There are a series of rapid precipitation synthesis reactions between the orthophosphoric acid and a certain metal, in the presence of calcium carbonate at room temperature [5].

To synthesize the cyclotetraphosphates of divalent metals we used various methods, such as: the thermal method, the hydrothermal method or the decomposition of dihydrogenophosphates of divalent metals $\text{M}_2\text{A}_y(\text{H}_2\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$. Those methods allow the partial replacement of divalent metallic cations with cheaper divalents that may enhance the properties of the precursors. Relevant in that regard is the synthesis of binary cyclotetraphosphates in solution, because the change of ratio between the metallic cations practically influences the optical, photochemical and thermal properties of the pigment. Thus, the cobalt and iron pyrophosphate (CoFe_2O_7) and the cobalt and iron cyclotetraphosphate ($\text{CoFe}_4\text{O}_{12}$) were synthesized by mixing CoCO_3 with Fe and H_3PO_4 , the former in a methanol-water solution and the latter by the same method, but in acetone-water solution, at room temperature. In both cases the obtained precursor was pale-pink. In that case the reactants in the precipitation medium have a serious effect on the morphology of the binary cyclophosphate of divalent metals and are in compliance with the phosphate groups presented in the coordination sphere [6].

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Usually, for the synthesis of the precursors obtained by substitution of Me^{2+} in various chromophore structures we used two procedures: a classical one, based on the calcination of the mechanically mixed oxide and/or salts and the highly exothermal synthesis by redox calcination, between the nitrates of certain metals and organic reduction compounds [7]. Thus, a frequently used pigment synthesis procedure, is to redox calcinate precursors as gel and micro-emulsions, or polymeric precursors, by employing citric acid as a reduction agent and various metallic nitrates as oxidants [8]. The *Pechini lab* synthesis procedure (for polymeric precursors) is also known and also the spinel type pigments, which are based on sol-gel processes [9].

In regard to the classical procedure, we should mention the synthesis of spinel pigments based on Cu-Mn-Cr, which takes place in two stages: first we obtained the intermediary product, by mixing the metallic oxides at medium temperature and then we performed the classical calcination in an electric oven. We also know the procedure by which to obtain spinel pigments through precipitation in a aqueous solution of mixed salts: MnCO_3 , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ and Na_2CO_3 . The main advantage of that procedure is that the size and shape of the pigment granules can be controlled according to the reaction conditions, such as the number and order of the reactants added, the pH, the agitation speed and the reaction temperature. The spinel pigment with the formula $\text{Cu}_{2.3}\text{Mn}_{2.8}\text{Cr}_{4.9}\text{O}_x$ provides intense shades of black [10].

Another method to synthesize a spinel pigment is the reaction of mechanically mixed metallic oxides in a solid state. In order to be complete, the reaction needs a temperature of approximately 1300°C or above, which has to be maintained for long periods of time. To process spinel pigments at an industrial scale, they use the method of precipitation in aqueous solution of the raw substances [11].

The organo-metallic precursors based on Co(II) and Zn(II), with various molar Co/Zn ratios, were used to synthesize colored spinel structures, which are used as painting materials (pigments) [12].

Relevant publications [13] also present an alternative method, consisting of the calcination of double layered hydroxides (LDHs). In that case, the cations can easily be exchanged, thus modifying the molar ratio of bivalent/trivalent metals in a broad manner and also the anions of the intermediary layer. For example, to prepare LDHs based on Co(II) you use microwave ovens for heating, a procedure that allows a fine control of the particle granulometry and avoids the formation of Co(III) species. Moreover, it is known that the Zn^{2+} cations behave as structure modifiers and may set the color of the pigment more precisely.

Another promising procedure [15] consists of the coprecipitation of solid or melted hydroxides, with subsequent separation thereof from the solution, followed by washing, drying and calcination of the resulted precipitates. A major advantage of that procedure is that the metallic hydroxides interact during coprecipitation and form a hydrocomplex "pre-structure" that leads, by precipitation, to the formation of stable amorphous structures, with a controlled granulation. Thus, the "pre-structures" easily transform into the finite product at a lower temperature and in a shorter period of thermal treatment. Consequently, such a technology has a series of advantages over the other two groups of pigment processing technologies (by thermal diffusion in solid or melted state

and the precipitation in protolythic solutions), but also certain disadvantages linked to corrosion and toxicity.

Systematic studies [16] revealed that the method of coprecipitation of metallic hydroxides is much more promising for the synthesis of ceramic pigments, because it provides pigments with a high degree of dispersion of the chromophore parameters in the volume phase of the granule and it lowers heat consumption (the pigment synthesis by that procedure requires temperatures between 100 and 200°C, much lower than other traditional syntheses by thermal diffusion in melted state or by hydrothermal precipitation in solutions).

The traditional method to synthesize orange ceramic pigments based on rutile, involve, apart from the solid state reaction of the precursors, a process of division by grinding, in order to adjust the granulometry of particles to the optimal size and causing a color enhancement. Moreover, by high division it is produced a better diffusion in the painting binder or in the coating matrix for mosaics and painted glass [17 - 19].

The properties of the chromophore pigments depend very much on their initial composition. Thus, Co^{2+} may be used to obtain pigments of black, dark gray, or dark brown. The introduction of Ni^{2+} confers pigments a dark green color and shades of Veronese green, due to the presence of the $[\text{NiO}_4]$ or Ni_2SiO_4 chromophores.

X-ray analysis revealed that the crystal phases are more intense when precipitation in liquid solutions is employed [20].

With the exception of procedures in solid phase by thermal diffusion, which require a lot of energy, the technologies of obtaining pigments by precipitation in aqueous solutions studied by us, included the following operations: preparation of the initial solutions, volumetric dosage, addition of the precipitation reactive agent, separation of the precipitate from the forming solution, washing the precipitate, drying/searing, calcination, grinding, packaging [21].

The present study aimed to establish the optimal conditions to synthesize new pigments based on phosphates and chromates, by coprecipitation in aqueous systems, at normal temperatures, in order to obtain polychrome pigments for mosaics and painted glass, as well as for water-based and oil-based paints. Moreover, we present a chemical and morphological characterization based on our SEM-EDX and micro-FTIR analysis of the processed powders, with additional notes in regard to their thermal and photo-chemical stability, which may indicate their possible application to obtain artistic polychrome systems for three purposes: polychrome coating systems for artistic mosaics and painted glass, pigments for oil based paints and pigments for water based paints.

Experimental part

Pigment Synthesis and Indexing

In the synthesis of the new, phosphate and chromate based pigments, with different shades than the commercially known ones, we used competitive systems of two or more precipitation reactions, mainly acid-base ones, assisted or not by redox and complexation processes. As processing procedure we employed co-precipitation in an aqueous solution of the chemical compounds, followed by filtration, washing, filtering, drying, calcination and fine mortaring.

We applied two reaction subsystems, starting from:

-chromophore precipitation anions (CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$ and PO_4^{3-}), that also contain soluble species as compensatory cations (H^+ , Na^+ , K^+ sau NH_4^+), and

-precipitation cations (Zn^{2+} , Co^{2+} , Co^{3+} , Fe^{2+} , Fe^{3+} , Mn^{2+} , Ni^{2+} and Bi^{3+}), that contain the soluble or partially soluble compensatory anions (Cl , HO , NO_3 , SO_4^{2-} etc.).

During synthesis we used a series of transitional metal cations in stable oxidation states (Zn^{2+} , Co^{2+} , Co^{3+} , Fe^{2+} , Fe^{3+} , Mn^{2+} , Mn^{3+} and Ni^{2+}) and one from the "p" block (Bi^{3+}), which, as a result of competitive reactions formed hardly soluble products with chromophore precipitation anions (CrO_4^{2-} , $Cr_2O_7^{2-}$ and PO_4^{3-}) and also some other products which formed in the reaction medium (Cl , HO and/or SO_4^{2-}). For example, hardly soluble products as neutral or acid salts were formed in acid mediums, whereas in neutral mediums and especially in alkaline ones the obtained pigments contained mixed or double hydrated oxides, oxohydroxides, oxosalts, or hydroxo/aquo coordination compounds. The base reactions are acid-basic, redox or complexation ones, as such, or in co-assistance systems, in pairs.

During our study, each pigment was indexed as "P", followed by a number corresponding to their synthesis order, in groups.

The precipitation anions employed in the synthesis of the seven groups of pigments were: CrO_4^{2-} (in the alkaline medium), $Cr_2O_7^{2-}$ (in the acid medium), and PO_4^{3-} (both acid and alkaline media), but the cations employed were different for each group and the reaction medium also differed according to pigment, 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: $Cr_2O_7^{2-}$ 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_4^{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_4^{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: $Cr_2O_7^{2-}$ and PO_4^{3-}).

The synthesis procedure for the 18 pigments was similar and was based on processes of co-precipitation by mixing with a rod in a gently shaken Berzelius 150 mL recipient with a solution of chromophore anions, in neutral, mild acid, or alkaline medium (according to case), The concentration ranged between 1.5 and 2M, over which we added 100mL of precipitation cations with the following concentrations: 1.5 M(**P1**), 2.6 M(**P2**), 2.5 M(**P3**), 2.3 M(**P4**), 2.0 M(**P5**), 2.5 M(**P6**), 2.2 M(**P7**), 2.0 M(**P8**), 2.5 M(**P9**), 2.0 M(**P10**), 1.8 M(**P11**), 2.0 M(**P12**), 2.5 M(**P13**), 2.5 M(**P14**), 2.3M(**P15**), 1.8 M(**P16**), 1.5 M(**P17**) and 2.7 M(**P18**).

The solution was added slowly, controlling the pH and temperature ($23 \pm 2^\circ C$), while function of the consistency of the precipitate, the shaking was continuous or discontinuous, with pauses of 2-3 min. After the precipitate stabilization in the reaction medium, the precipitation was checked.

After complete coprecipitation of the micro-dispersed system was left to stabilize and after decantation the precipitate was extracted with a small amount of water and was filtered. Additional washing with distilled water was done on a filter. After filtration, the precipitate was set in a porcelain capsule and was dried at room temperature. The dried product was stored in plastic, airtight bags, from which we took samples for analysis and a series of practical experiments to assess their application to polychrome artistic elements.

The SEM-EDX Analysis

The newly synthesized pigments were studied from the point of view of their morphology and granulometry of their particles, as well as in regard to the elements in their composition, by SEM-EDX method. The data obtained were correlated with those from the micro-FTIR spectroscopy.

As mentioned before, the SEM-EDX technique is a very useful instrument for the study of pigments and other mineral or organic materials that may be found in a painting [27].

For our analysis we used an electronic microscope with scanning SEM, VEGA II LSH, made in The Czech Republic, coupled with a QUANTAX QX2 EDX detector, made in Germany.

The microscope, entirely controlled by computer, has an electron gun with a tungsten filament and can obtain a resolution of 3nm at 30kV and a zoom range from 30X to 1,000,000X in the "resolution" mode, the acceleration tension ranging from 200 V to 30 kV and the scanning speed from 200 ns to 10 ms per pixel. Its working pressure is lower than 1×10^{-2} Pa. The image obtained may consist of secondary (SE) or back-scattered (BSE) electrons.

The technology used, together with the visualization of the micro-photogram, allows image rendering with the location of the atoms on the surface under analysis and based on the X-ray spectrum one can determine the elements composing a certain microstructure, or a selected area (in gravimetric or molar percents) and evaluate variations in the composition.

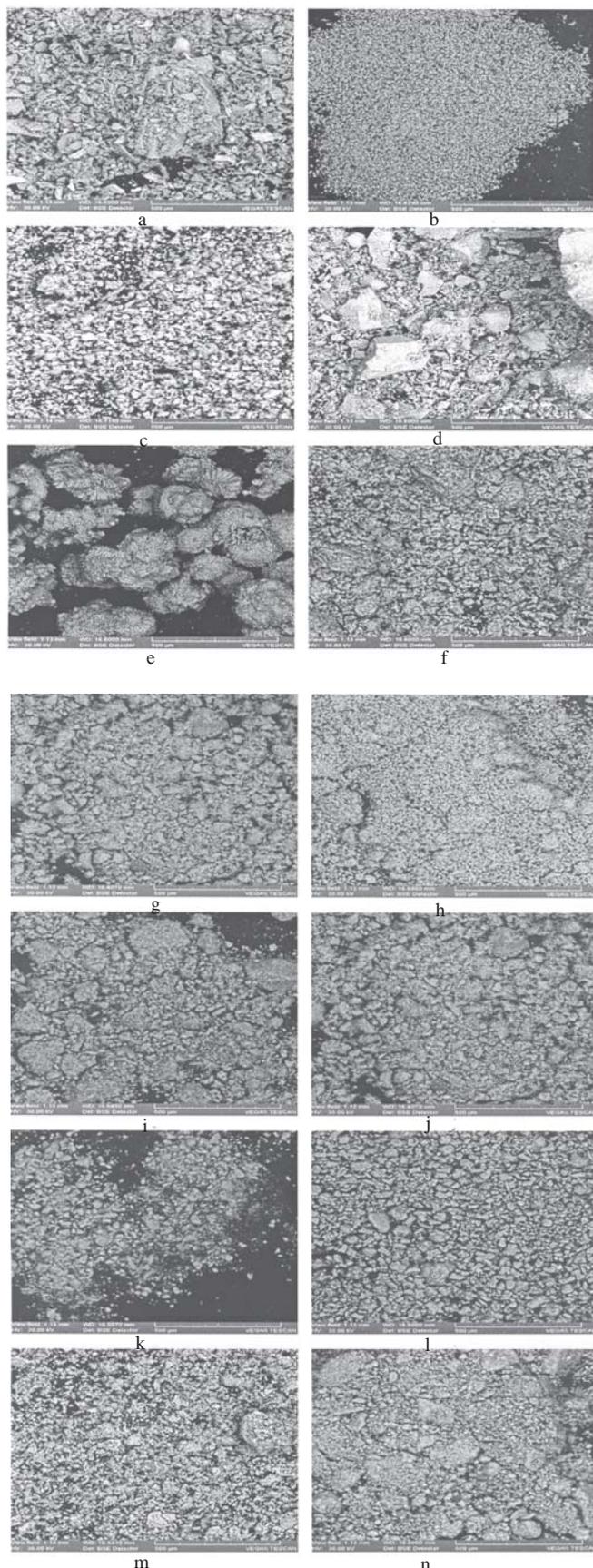
The Micro-FTIR Analysis

The FT-IR spectra were recorded with a FT-IR spectrophotometer coupled with a HYPERION 1000 microscope, both made in Germany. They allowed a noninvasive analysis of the powder samples, by reflection.

The software used was OPUS/VIDEO, for interactive video data collection. The detector was of the MCT type, cooled with liquid nitrogen (-196°C).

The spectral analysis domain was 600-4000 cm^{-1} and the measured area ranged from 20 to 250 μm , the microscope having a 10X lens.

The software recorded the spectrum after a 32x scanning process and the structural components were selected based on a repository of spectra.



Results and discussions

Figure 1 presents the SEM micro-photographs and table 1 lists the concentrations in atomic percentage of the chemical elements in the composition of the 18 newly synthesized pigments. Assessments were made according to the EDS spectra, with a dedicated SEM-EDX software. Different colours were chosen by convention.

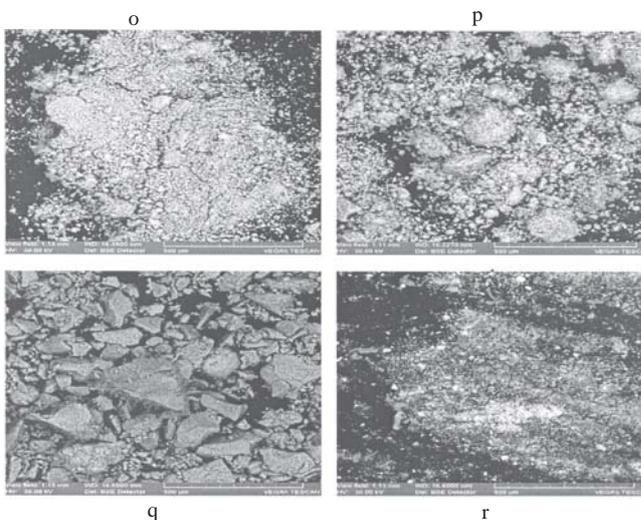


Fig. 1. SEM images of the pigments: a - P1, b - P2, c - P3, d - P4, e - P5, f - P6, g - P7, h - P8, i - P9, j - P10, k - P11, l - P12, m - P13, n - P14, o - P15, p - P16, q - P17, r - P18

The SEM images revealed that the morphology of the newly synthesized 18 pigment powders may be classified according to three granulometric classes.

-fine grains with small and medium crystals, slightly rounded (**P2, P3, P6, P7, P9, P10**), synthesized in alkaline medium;

-medium and variably sized grains, with small and medium crystals, slightly rounded (**P8, P12, P13, P14, P15 and P16**), synthesized in neutral and alkaline medium;

-large grains, with medium and large granules, rough, frail (**P1, P4, P5, P11, P17 and P18**), with the exception of **P5**, which has rounded crystals. These pigments were synthesized in a mild acid or neutral medium.

An important role in the morphology and granulometry of the powders is played by the pH in the precipitation medium, from synthesis to the calcination stage.

The P1 pigment was set as reference, as it has the simplest composition.

Figure 2 presents the micro-FTIR spectra, which reveal the congruent phases in the deep structure of the pigments.

According to the molar synthesis ratios, correlated with the data in table 1 and the FTIR spectra in figure 2, we could identify the species formed in the composition of the pigments.

Thus, for the reaction system of the **P1** pigment, only one hardly soluble species formed: $\text{Zn}_3(\text{PO}_4)_2$. In the reaction system of the **P2** pigment the following hardly soluble molecular species were formed: ZnCrO_4 , $\text{Zn}_3(\text{PO}_4)_2$ and a large quantity of $\text{Zn}_2\text{O}(\text{OH})_2$.

In the reaction system of the **P3** pigment the following hardly soluble species were formed: ZnCrO_4 , MnCrO_4 , $\text{Zn}_3(\text{PO}_4)_2$, $\text{Mn}_3(\text{PO}_4)_2$, $\text{Zn}_2\text{O}(\text{OH})_2$, and $\text{Mn}_2\text{O}(\text{OH})_2$; for **P4** there were formed ZnCrO_4 , $\text{Zn}_3(\text{PO}_4)_2$, MnCrO_4 and $\text{Mn}_3(\text{PO}_4)_2$; for **P5** ZnCrO_4 , $\text{Zn}_3(\text{PO}_4)_2$, MnCrO_4 , $\text{Mn}_3(\text{PO}_4)_2$ and $\text{CrO}(\text{OH})_2$, as confirmed by the EDX and FTIR spectra of those pigments.

Table 1
CHEMICAL COMPOSITION OF THE 18 PIGMENTS ACCORDING TO THE EDX SPECTRA

Pigment		Chemical composition in atomic percentage (%)									
		Zn(II)	Cr(VI)	P(V)	O(II)	Mn(II)	Fe(II)	Fe(III)	Co(II)	Ni(II)	Bi(III)
P.1.	T. (%)	35.20	-	19.00	42.63	-	-	-	-	-	-
	P. (%)	32.75	-	17.69	39.67	-	-	-	-	-	-
P.2.	T. (%)	61.26	0.77	4.55	30.43	-	-	-	-	-	-
	P. (%)	59.80	0.75	4.44	29.71	-	-	-	-	-	-
P.3.	T. (%)	27.98	5.60	8.43	32.66	23.33	-	-	-	-	-
	P. (%)	27.83	5.57	8.38	32.48	23.21	-	-	-	-	-
P.4.	T. (%)	39.84	11.77	1.94	16.53	37.32	-	-	-	-	-
	P. (%)	36.85	10.89	1.80	15.29	34.52	-	-	-	-	-
P.5.	T. (%)	23.28	11.69	9.42	31.70	16.93	-	-	-	-	-
	P. (%)	23.07	11.59	9.33	31.42	16.78	-	-	-	-	-
P.6.	T. (%)	35.33	6.82	6.95	27.31	-	28.12	-	-	-	-
	P. (%)	34.32	6.63	6.75	20.16	-	19.59	-	-	-	-
P.7.	T. (%)	31.65	15.01	10.45	29.40	-	23.23	-	-	-	-
	P. (%)	30.31	14.62	10.18	28.64	-	22.63	-	-	-	-
P.8.	T. (%)	19.60	-	8.63	29.72	-	27.58	-	-	-	-
	P. (%)	19.09	-	8.27	28.46	-	26.41	-	-	-	-
P.9.	T. (%)	5.31	5.37	17.27	29.41	-	-	38.53	-	-	-
	P. (%)	5.11	5.17	16.70	28.30	-	-	37.07	-	-	-
P.10.	T. (%)	18.94	7.35	13.19	34.09	-	-	20.54	-	-	-
	P. (%)	18.41	7.15	12.82	33.14	-	-	19.96	-	-	-
P.11.	T. (%)	12.94	1.07	16.87	31.59	-	-	33.18	-	-	-
	P. (%)	12.80	1.06	16.62	31.27	-	-	32.84	-	-	-
P.12.	T. (%)	39.59	-	17.18	33.58	-	-	-	9.88	-	-
	P. (%)	38.50	-	16.71	32.65	-	-	-	9.61	-	-
P.13.	T. (%)	19.61	16.58	6.94	26.74	-	-	-	23.34	-	-
	P. (%)	19.53	16.52	6.91	26.64	-	-	-	23.25	-	-
P.14.	T. (%)	33.58	5.73	13.90	33.54	-	-	-	-	9.94	-
	P. (%)	32.27	5.51	13.36	32.23	-	-	-	-	9.55	-
P.15.	T. (%)	-	2.51	17.19	33.66	-	-	-	-	44.91	-
	P. (%)	-	2.47	16.90	33.09	-	-	-	-	44.15	-
P.16.	T. (%)	30.90	10.42	11.96	26.57	-	-	-	-	13.58	-
	P. (%)	30.15	10.17	11.67	25.92	-	-	-	-	13.24	-
P.17.	T. (%)	30.50	9.00	13.25	27.06	-	-	-	-	12.61	-
	P. (%)	30.31	8.95	13.17	26.89	-	-	-	-	12.53	-
P.18.	T. (%)	2.42	8.36	2.16	51.67	-	-	-	-	-	44.62
	P. (%)	2.16	7.48	1.94	46.22	-	-	-	-	-	39.92

In the reaction system of the **P6** pigment there were formed the following hardly soluble species: $ZnCrO_4$, $Zn_3(PO_4)_2$, $Fe_2(CrO_4)_3$, $FePO_4$, $Zn_2O(OH)_2$ and $FeO(OH)$; for **P7** there were formed: $ZnCrO_4$, $Zn_3(PO_4)_2$, $Zn_2O(OH)_2$, $FeCrO_4$, $FePO_4$, $FeO(OH)$ and $CrO(OH)$; and for **P8** there were formed: $Zn_3(PO_4)_2$, $Zn_2O(OH)_2$, $FePO_4$ and $FeO(OH)$, as confirmed by their EDX and FTIR spectra.

In the reaction system of the **P9** pigment the following hardly soluble species were formed: $ZnCrO_4$, $Zn_3(PO_4)_2$, $Zn_2O(OH)_2$, $FeCrO_4$, $Fe_3(PO_4)_2$ and $FeO(OH)$; for **P10** there were formed: $ZnCrO_4$, $Zn_3(PO_4)_2$, $Zn_2O(OH)_2$, $FeCrO_4$, $Fe_3(PO_4)_2$ and $FeO(OH)$; for **P11**: $ZnCrO_4$, $Zn_3(PO_4)_2$, $FeCrO_4$, $Fe_3(PO_4)_2$, $Zn_2O(OH)_2$ as confirmed by their EDX and FTIR spectra.

In the case of **P12**, the reducing cation Co^{2+} , requires for its oxidation to Co^{3+} a -1.808 V potential and in the reaction system there will form the following molecular species: $Zn_3(PO_4)_2$, $Zn_2O(OH)_2$, $CoPO_4$, and $CoO(OH)$; for **P13** there were formed: $ZnCrO_4$, $Zn_3(PO_4)_2$, $CoPO_4$ and $Co_2(CrO_4)_3$, as confirmed by their EDX and FTIR spectra.

In the reaction system of the **P14** pigment the reducing cation Ni^{2+} oxidized to Ni^{3+} and the following species formed: $ZnCrO_4$, $Zn_3(PO_4)_2$, $Zn_2O(OH)_2$, $Ni_2(CrO_4)_3$, $NiPO_4$ and $NiO(OH)$; for **P15** there were formed: $Ni_2(CrO_4)_3$, $NiPO_4$ and $NiO(OH)$; for **P16** and **P17** there were formed: $ZnCrO_4$, $Zn_3(PO_4)_2$, $Ni_2(CrO_4)_3$, $NiPO_4$ as confirmed by their EDX and FTIR spectra.

In the reaction system of the **P18** pigment there were formed the following hardly soluble species: $BiPO_4$, $Bi_2(CrO_4)_3$, $ZnCrO_4$ and $Zn_3(PO_4)_2$, as confirmed by its EDX and FTIR spectra.

The collected chemical data and the procedure of fine synthesis confirmed the co-precipitation of the chemical components. The following figures present the distribution maps for the characteristic elements of the newly synthesized pigments, represented in different colors by convention.

The SEM analysis of the 18 pigments allowed us to conclude that they were formed of small particles or grains of various sizes, some rounded and some roughly shaped. On the whole, their morphologies were quite homogeneous and there were no notable differences in the intensity or contrast of the samples.

EDX analyses of different regions of each sample were made for a quantitative characterization of their homogeneity.

According to the data collected we determined that the samples have a good dispersion of the molar ratio for the composing elements of each pigment.

As observed in table 1, the chemical compositions of the pigments are similar to their theoretical ones.

In some cases there are differences from the theoretical composition (stoichiometry) of the pigments, possibly

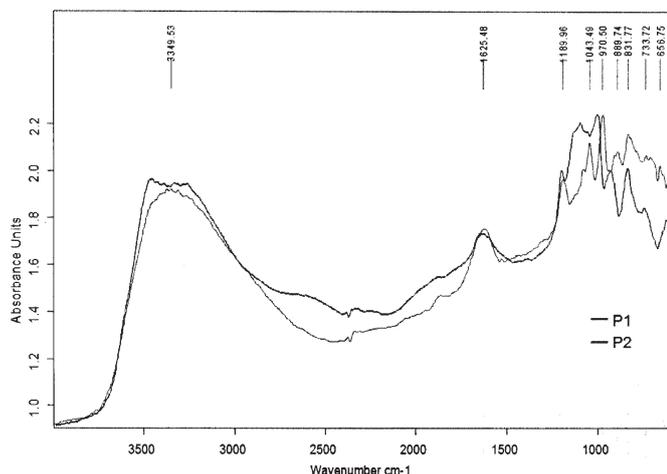


Fig. 2. The micro-FT-IR spectra for the pigments based on Zn(II) phosphate – **P1** and Zn(II) chromate and phosphate – **P2**

caused by a partial precipitation or by an incomplete homogenization of the metal species in liquid phase, during the synthesis of the pigment samples.

Those analyses indicated an almost homogeneous composition of the samples throughout their entire mass.

The micro-FTIR Analysis

For their spectrophotometric IR characterization the pigments were dried at $110 \pm 5^\circ\text{C}$ for 4 h. We used the group characteristic vibrations of the main structural components in the process.

Thus, figure 2 presents the micro-FT-IR spectra of pigments **P1**, based on Zn(II) phosphate and of **P2**, based on Zn(II) phosphate and chromate. The spectrum of **P1** was taken as reference for the spectra of the other pigments.

In the domain of waters (hygroscopic water, hydration network water, hydrogels and chemically bound water in the hydroxilic groups, or hydro-compounds) between 3600 and 3200 cm^{-1} , the spectra present a large set with significant peaks at 3448 cm^{-1} for P1 and at 3349 cm^{-1} , for P2 and then another wide set at $1630\text{--}1600\text{ cm}^{-1}$, with a significant peak at 1628 cm^{-1} for P1 and at 1625 cm^{-1} for P2. There are two sets specific to hydro-compounds of Zn (II), two sets corresponding to the $1190\text{--}1000\text{ cm}^{-1}$ and $1000\text{--}900\text{ cm}^{-1}$ domains, with significant peaks at 1189, 1087, 993 and 920 cm^{-1} for P1 and at 1189, 1043 and 970 cm^{-1} for P2, specific to the PO_4^{3-} ion, the set specific to the $970\text{--}770\text{ cm}^{-1}$ with significant peaks at 831 and 889 cm^{-1} corresponding to the chrome ion CrO_4^{2-} are only found in P2.

In the $900\text{--}600\text{ cm}^{-1}$ domain, specific to the Me-O links, for P1 there is a single set with a peak at 826 cm^{-1} and for P2 there are two peaks at 773 and 656 cm^{-1} . Here we find part of the peaks specific to Zn-O

Figure 3 presents the micro-FT-IR spectra of pigments P3, P4 and P5 based on Zn(II) and Mn(II) phosphates and chromates. Those pigments have a wide and strong absorption, specific for various water types in the $3600\text{--}3200\text{ cm}^{-1}$ range, with significant peak at 3415 cm^{-1} for the P3 pigment, at 3386 cm^{-1} for P4 and at 3430 cm^{-1} for the P5 pigment.

Within the $1350\text{--}1600\text{ cm}^{-1}$ range there are three representative peaks, specific for aqueous hydrocomplexes and Zn(II) and Mn(II) oxi-salts. The first peak, specific for Zn(II) oxi-salts, the most significant in that group, was found at 1643 cm^{-1} for P3, at 1648 cm^{-1} for P4, and at 1649 cm^{-1} for the P5 pigment, after which there are two other peaks,

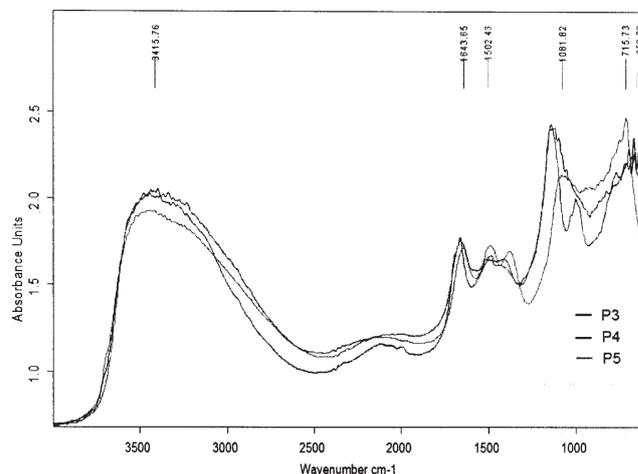


Fig. 3. Micro-FT-IR spectra for the Zn(II) and Mn(II) phosphate and chromate pigments, labeled **P3**, **P4** and **P5**

narrow ones as well, specific to Mn(II) oxi-salts, quite significant in the P3 pigment and not so much in the other two (P4 and P5), with representative peaks at 1502 cm^{-1} and at 1350 cm^{-1} , with the mention that at P4, the last one shifts towards numbers of a slightly higher wave.

Within the $1190\text{--}1000\text{ cm}^{-1}$ range and the $1000\text{--}900\text{ cm}^{-1}$ one, specific to the PO_4^{3-} phosphate ion, there are two significant peaks at 1081 cm^{-1} for P3 pigment, and at 1110 cm^{-1} for P4, then at 1133 and 989 cm^{-1} for P5. The $960\text{--}770\text{ cm}^{-1}$ range, specific to the CrO_4^{2-} chromed ion, with an elevated peak at 715 cm^{-1} for P3 pigment, slightly dimmed for P5 and moved to 759 cm^{-1} for P4.

For the $900\text{--}600\text{ cm}^{-1}$ range, specific to Me-O (Zn-O and Mn-O) bonds, we encountered again peaks at 685 and 658 cm^{-1} for the P4 pigment and at 698, 672, 650 and 628 cm^{-1} for P5. The P3 pigment lacks the peaks specific to Zn-O and Mn-O.

Taken as an example for the other newly synthesized pigments, the same spectral domains of the micro-FT-IR spectra from the first two readings will be used in discussions.

The following three pigments, based on Zn(II) and Fe(II) phosphate and chromate, labeled P6, P7 and P8, as presented in figure 4, have most of the significant peaks that were found at the first five ones.

The water domains, as an extended absorption band ranging from $3600\text{ to }3200\text{ cm}^{-1}$, have a significant peak at 3466 cm^{-1} for P6 pigment, at 3403 cm^{-1} for P7 and at 3329 cm^{-1} for P8.

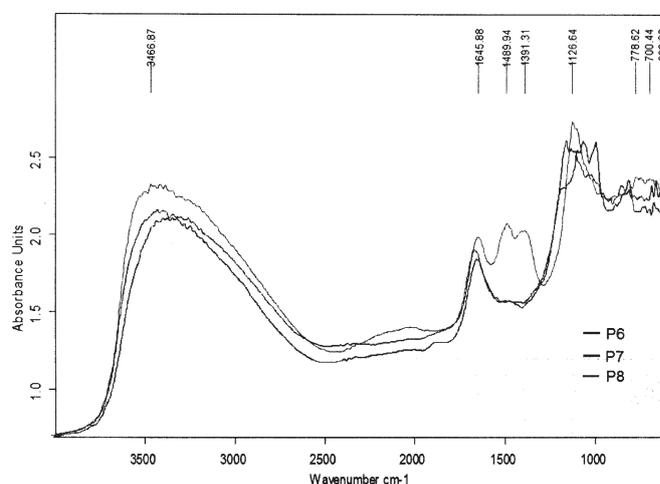


Fig. 4. The micro-FT-IR spectra for Zn(II) and Fe(II) phosphate and chromate pigments, labeled **P6**, **P7** and **P8**

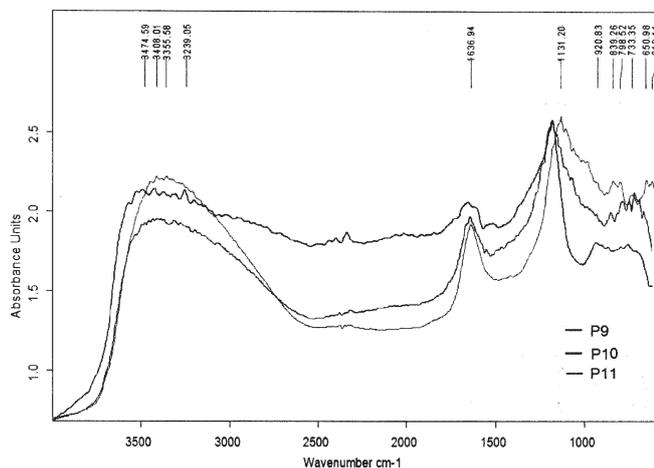


Fig. 5. The micro-FT-IR spectra for Zn(II) and Fe(II) phosphate and chromate pigments labeled **P9**, **P10** and **P11**

For the 1350-1600 cm^{-1} range, there are three representative peaks, specific to aqua, hydrosystems and Zn(II) and Fe(II) oxysalts. The first peak, specific to Zn(II) oxysalts, which is the most significant of this group, was found at 1641 cm^{-1} , for P6, at 1645 cm^{-1} , for P7, and at 1637 cm^{-1} for P8. After that there are other peaks, also narrow ones, specific to Fe(II) oxysalts, strongly highlighted in P7 and much less in the other two (P6 and P8).

There are two lanes, corresponding to the 1180-1000 cm^{-1} range and the 1000 – 900 cm^{-1} one, with significant peaks at 1126 cm^{-1} for P6 and at 1049 and 978 cm^{-1} for P8, specific to the PO_4^{3-} ion; a corresponding lane in the 960-770 cm^{-1} range with a peak at 778 cm^{-1} for P7, at 827 cm^{-1} for P6 and at 797 cm^{-1} for P8, specific to the CrO_4^{2-} chromed ion. Then a lane, corresponding to the 900-600 cm^{-1} range, follows with peaks at 700 and 623 cm^{-1} for P7, at 661 and 637 for P6 and at 706 and 657 cm^{-1} for P8, specific to the Zn-O and Fe-O area. The complexity of peaks within the 1100-600 cm^{-1} domain is enhanced by the presence of iron.

In figure 5 the micro-FT-IR spectra of P9, P10 and P11, based on Zn(II) and Fe(III), are shown.

Again, we found the same wide and strong absorption specific to water and hydro-systems in the 3600-3200 cm^{-1} range, with specific peaks at 3355 cm^{-1} , for P9, at 3474, 3408 and 3239 cm^{-1} , for P10, and at 3406 cm^{-1} for P11, but different from pigments with Fe(II). Then there is a wider lane in the 1700-1600 cm^{-1} range, with significant peaks at 1636 cm^{-1} , for P9, at 1638 cm^{-1} , for P10 and at 1638 cm^{-1} for P11. Also, the other two following ranges are different from those of Fe(II) pigments, both in intensity, but also from the peak complexity point of view. Thus, within the 1180-1000 and 1000-900 cm^{-1} ranges, specific to the PO_4^{3-} ion, we found significant peaks at 1131 cm^{-1} , for P9, at 1164 and 900 cm^{-1} , for P10, and at 1174 cm^{-1} , for P11. In the 960-770 cm^{-1} range, specific to the CrO_4^{2-} chrome ion, we find again the peaks at 839 and 798 cm^{-1} , for P9 and P10, at 848 and 786 cm^{-1} , for P11. The last range, between 900 and 600 cm^{-1} , specific to Zn-O and Fe-O, has peaks at 733, 650 and 619 cm^{-1} in P9, at 740 cm^{-1} for P10 and for P11 at 744, 716 and 663 cm^{-1} .

Figure 6 shows the micro-FT-IR spectra of pigment P12 and P13, based on Zn(II) and Co(II) phosphate and chromate, that have the same wide, intense absorption in the 3600-3200 cm^{-1} range, with a significant peak at 3338 cm^{-1} for P12 and at 3385 cm^{-1} for P13.

The next band, this time, is very narrow. In the 1700-1600 cm^{-1} range there is a significant peak at 1626 cm^{-1} for

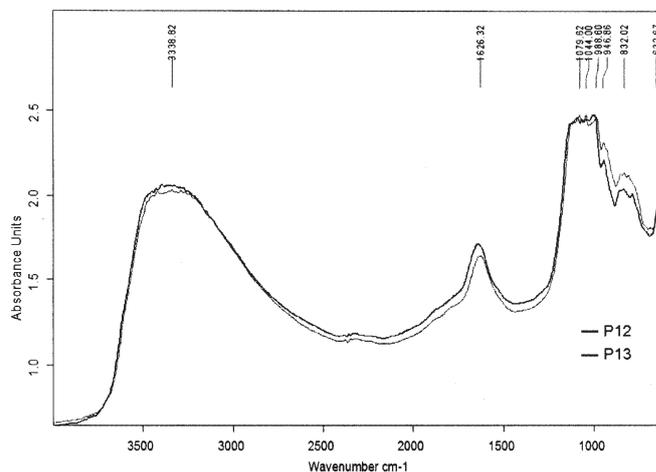


Fig. 6. The micro-FT-IR spectra for Zn(II) and Co(II) phosphate and chromate pigments labeled **P12** and **P13**

P12 and at 1633 cm^{-1} for P13. The other two lanes, specific for the PO_4^{3-} ion, corresponding to the 1180-1000 cm^{-1} and 1000-900 cm^{-1} ranges have significant peaks at 1079, 1044 and 988 cm^{-1} for P12 and at 1080 and 996 cm^{-1} for P13. The chrome ion lane from the 960-770 cm^{-1} range has peaks at 946 and 832 cm^{-1} for P12 and 936 and 827 cm^{-1} for P13. The last range, the one between 900 and 600 cm^{-1} has a peak at 630 cm^{-1} for P12 and at 632 cm^{-1} for P13.

In Figure 7 and 8 the micro-FT-IR spectra of the Zn(II) and Ni(II) phosphate and chromate pigments are shown. They were labeled P14, P15, P16 and P17, the first two precipitated in a base medium and the other two in a neutral medium, less favourable to washing purification.

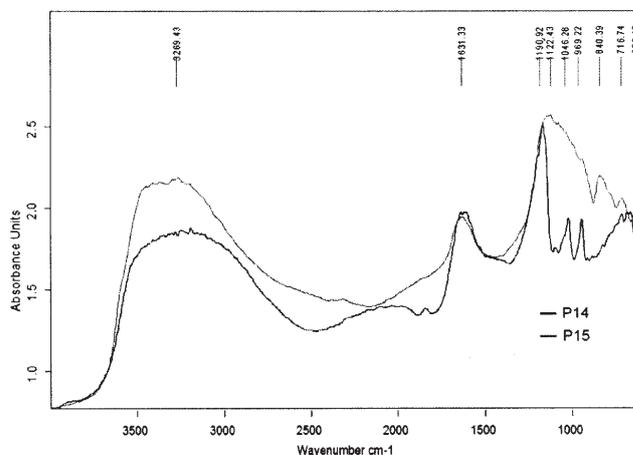


Fig. 7. The micro-FT-IR spectra for Zn(II) and Ni(II) phosphate and chromate pigments labeled **P14** and **P15**

In the 3600-2700 cm^{-1} range there is a significant peak at 3269 cm^{-1} for P14, another at 3215 cm^{-1} for P15, one at 3383 cm^{-1} for P16 and two at 3189 and at 3063 cm^{-1} for P17. The complexity of this band for P17 may be explained by a weak purification by washing of the deposit.

The second group of absorption band is the one from the 1700-1600 cm^{-1} range, with significant peaks at 1631 cm^{-1} for P14, at 1600 cm^{-1} for P15, at 1610 cm^{-1} for P16, and at 1695 cm^{-1} for the last pigment, P17.

The third range, specific to the phosphate ion, the one for the 1180-1000 cm^{-1} and 1000-900 cm^{-1} lanes had significant peaks at 1122 cm^{-1} for P14, at 1190, 1119 and 1046 cm^{-1} for P15, at 1051 cm^{-1} for P16, at 1166 and 1000 cm^{-1} for P17.

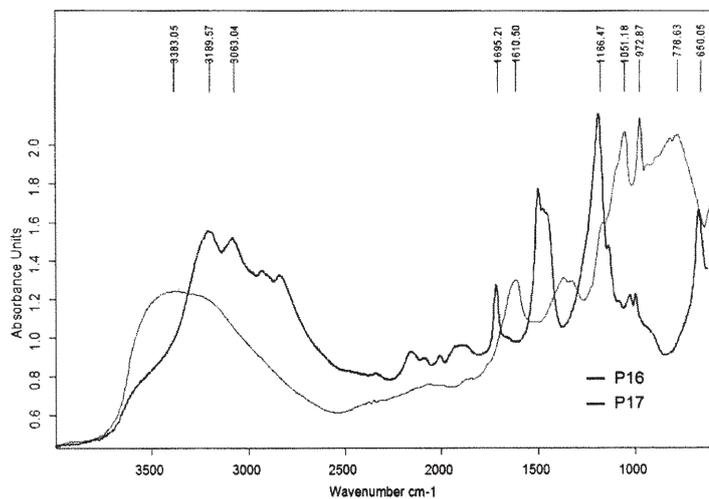


Fig. 8. The micro-FT-IR spectra for Zn(II) and Ni(II) phosphate and chromate pigments labeled **P16** and **P17**

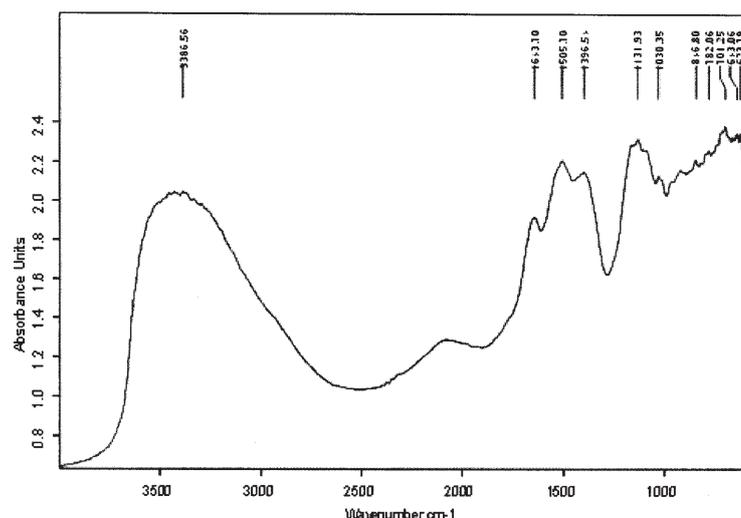


Fig. 9. The micro-FTIR spectrum for the Zn(II) and Bi(III) phosphate and chromate pigment, labeled **P18**

The fourth range, between 960 and 770 cm^{-1} , specific to the chromate ion had a peak at 840 cm^{-1} for P.14, at 969 cm^{-1} for P.15, at 972 cm^{-1} for P.16, and at 976 cm^{-1} for P.17.

The fifth range, between 900-600 cm^{-1} , specific to the Zn-O and Ni-O chemical bonds, has the following peaks: at 716 and 630 cm^{-1} for P.14, at 738 and 688 cm^{-1} for P.15, at 778 cm^{-1} for P.16 and at 650 cm^{-1} for P.17.

Figure 9 shows the micro-FTIR spectrum of the last pigment, P.18, based on Zn(II) and Bi(III) phosphate and chromate. It has a wide, intense band in the 3600-3200 cm^{-1} range with a significant peak at 3386 cm^{-1} . We must note that at 2100 cm^{-1} there is a specific absorption band only for this pigment, for the congruent phase of the bismuth sub-phosphate.

The second range, between 1630-1390 cm^{-1} , has three significant peaks: at 1643 cm^{-1} , at 1505 cm^{-1} and at 1396 cm^{-1} , corresponding to the Zn(II) and Bi(III) oxy-salts.

The third range, between 1305 and 1105 cm^{-1} had a significant peak at 1131 cm^{-1} , specific to the PO_4^{3-} metaphosphate ion, then was a wider range, with three groups of bands. The one between 110 and 800 cm^{-1} had a significant peak at 1030 cm^{-1} and at 816 cm^{-1} , specific for the chrome ion and 700-600 cm^{-1} with significant peaks at 782, 701, 643 and 623 cm^{-1} , specific to the Zn-O and Bi-O bonds.

The micro-FTIR spectra confirm the composition of the 18 pigments determined by EDX and assess the purity degree of some of them.

Conclusions

We synthesized 18 thermally and photo-resistant pigments by precipitation in an aqueous system. The

pigments were based on zinc dichromate, chromate and phosphate chromophore anions, as basic precursors, and as precipitation cations, together with Zn^{2+} , the following cations were used: Mn^{2+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} and Bi^{3+} . They might be applied as such for oil paintings, or fritted for mosaics and stained glass.

After their synthesis in an aqueous-alkaline medium, separately neutral and separately mild acid (according to case), the deposits were washed, dried and calcinated, then the powders were analyzed by SEM-EDX and micro-FTIR. The results allowed the chromophore species involved in precipitation to be highlighted in the composition of the pigments. By correlating the molar ratios used for synthesis and the elemental chemical composition revealed by the EDX spectra, the main components from the synthesized pigments were marked and confirmed by the micro-FTIR analysis. The SEM micro-photographs revealed the morphology and granulometry of the powders.

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