

# Obtaining and Characterization of Ceramic Pigments for Polychrome Artistic Elements

## II. Microscopic and colorimetric analysis

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*The present paper deals with the microscopic and colorimetric characterization of 18 thermally and photo-resistant pigments, obtained by co-precipitation in an aqueous system, based on phosphate and zinc chromate chromophore structures, chemically doped with Mn(II), Fe(II), Fe(III), Co(II), Ni(II) and Bi(III) cations. The optical microscopic analysis and the measurements of colorimetric parameters (CIE L\*a\*b\*) were done on non-irradiated samples, as well on those irradiated with a UV lamp for 6, 8 and 12 h respectively, after being thermally treated at a temperature of 110°C for 4 h. Despite the fact they start from the same precursor (zinc phosphate and chromate), as a major processing phase in doping with chromophore cations, a large group of ceramic pigments was obtained, with different thermal and photochemical behaviour. Based on the experimental data, the 18 newly synthesized pigments were divided in two groups: those with high stability that can be used to manufacture polychrome elements for mosaics and stained glass and those that can be applied as fritted pigments for oil or water based paints.*

*Keywords: Inorganic pigment; Ceramic; Optical Microscopy; CIE L\*a\*b\* Colorimetry; Photo- and Thermal Stability*

There are many publications on colorimetric analysis and optical microscopy applied in the study of colour alteration and of ceramic pigment stability. Usually they focus more on the influence of chemical or physical doping of the precursors with chromophore cations and less on the influence of the thermal treatment or the UV irradiation. The following examples underline the type of approach used in such studies.

It is known that the CIEL\*a\*b\* space suggested by CIE in 1976 is used [1] in the colorimetric analysis by reflection, for the graphical representation of the colorimetric values of the pigments under analysis. Within that colorimetric space, the tint (represented by fundamental colours - red, green, yellow and blue), brightness or clarity (represented by the chromatic stimulus that varies from black to white) and saturation (purity of a colour) are expressed according to three coordinates: L\*, a\* and b\*. On the X axis the a\* parameter has values between red (a\* > 0) and green (a\* < 0) stimuli; on the Y axis the b\* parameter varies between yellow (b\* > 0) and blue (b\* < 0) stimuli and on the polar Z axis the L\* parameter represents the brightness (grey axis), varying between white and black (dark colours will have lower values towards black: 0.0;0.0;0.0; the origin of the Cartesian system (XYZ), labelled (50.0;50.0;50.0), the lighter colours or highly elevated values being expressed between origin (50.0;50.0;50.0) and white (≥ 100.0; ≥100.0; ≥100.0).

In agreement with [2-4] the colour difference parameters between the (T) sample and that of (R)

reference pigment are expressed by the mathematical equations:

$$\Delta a^* = a^*_T - a^*_R; \Delta b^* = b^*_T - b^*_R; \Delta L^* = L^*_T - L^*_R$$

Based on these equations the deviation or chromatic shifting can be calculated, as the geometrical distance between two positions in the CIE LAB colour space, as follows:

$$\Delta E^* = [\Delta a^{*2} + \Delta b^{*2} + \Delta L^{*2}]^{1/2}$$

Then, by using the values of the L\*, a\* and b\* parameters, the following parameters can be calculated:

-the saturation or purity difference, through the relation:

$$\Delta C^* = [a^{*2}_T + b^{*2}_T]^{1/2} - [b^{*2}_R + L^{*2}_R]^{1/2} \text{ and}$$

-the tint difference, through the relation:

$$\Delta H^* = [\Delta E^{*2} - \Delta L^{*2} - \Delta C^{*2}]^{1/2}.$$

For example [4] the intense blue-violet colour has for the b\* parameter negative values between -26.0 and -31.0 that correspond to the blue area, for the a\* parameter, positive values, between 9.0 and 11.0 that correspond to the red area, and the L\* parameter has rather reduced values, between 36.0 and 46.0, indicating dark colours of

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the samples within the XOY equatorial space. We should note that these values are very similar to those of the  $\text{Co}_3(\text{PO}_4)_2$  pigment, that is slightly darker, having the  $L^*/a^*/b^*$  values between 35.7/9.3/-27.6 and 37.2/11.3/-35.5. At a maximum doping with Mg and a minimum content of Co the pigment will have for the  $b^*$  parameter (responsible for the blue colour) a more negative value (between -35.0 and -33.0), the  $a^*$  parameter (for red) will drop towards the 6.0 value, while the  $L^*$  parameter has relatively elevated values (between 45.0 and 53.0). This pigment, obtained by maximum doping of the Co(III) phosphate with Mg(II) will be *intense blue*, which corresponds to the colorimetric values of  $L^*/a^*/b^* = 53.0/6.0/-33.0$ .

So, the intense blue-violet pigments, less toxic than the classic blue ceramic pigment,  $\text{Co}_3(\text{PO}_4)_2$ , were obtained by synthesizing, through co-precipitation in an aqueous system of Co and Mg diphosphates, resulting in less toxic pigments with the  $\text{Mg}_x\text{Co}_{3-x}(\text{PO}_4)_2$  formula.

Similar results were reached with the pigments obtained as solid Fe(III) and Co(II) phosphate solutions with  $\text{Co}^{\text{II}}\text{Fe}^{\text{III}}\text{PO}_4$  (that contains 12-20% of Co) and  $\text{Co}^{\text{II}}\text{Fe}^{\text{III}}\text{O}_{1-x}(\text{PO}_4)_{1+x}$  formula (that contains under 10% Co) [5].

A spinel type pigment was synthesized [6], with the  $\text{Cu}_{2.3}\text{Mn}_{2.8}\text{Cr}_{4.9}\text{O}_x$  formula, of intense black colour. Such a pigment synthesized in the temperature range between 700 and 900°C has values up to 4.0 for the  $b^*$  colorimetric coordinate. The appearance of  $\text{Cr}_2\text{O}_3$  at a lower temperature has a bad influence on the colour. The brightness value ( $L^*$ ) increases a little as the calcination temperature grows. It has been noticed that this value rises as the particle dimension grows. The green colour range affects only the value of the  $a^*$  coordinate, that decreases as the calcination temperature rises. These examples allowed researchers to draw the conclusion that sulphates are the optimum basic materials for synthesizing highly stable black spinel type pigments.

Another example [7] where colorimetric measurements were applied is the case of pigments based on CoO-ZnO, whose colorimetry was done after glazing out the pigments on white ceramic stands at approximately 950°C. Both colorimetric parameters,  $a^*$  and  $b^*$ , of the  $\text{Co}_x\text{Zn}_{1-x}\text{O}$  pigment, have similar values to those of pigments based on Co(II) silicate and aluminate. Thus, the CIE  $L^*a^*b^*$  diagram for that pigment has positive values between 2.00-12.64 for  $a^*$ , negative values between -19.93 and -33.41 for  $b^*$ , and a brightness between 28.43 and 52.27. These values are in agreement with the structural and spectroscopic analysis.

As seen so far, the brightness of a certain sample depends mainly on: the calcination temperature of samples and the nature and concentration of the chromophore cations used for doping the precursor. Thus, the effects on the brightness of the pigment obtained by chemical or physical doping with chromophore cations, different from those of the precursors, are felt even at a very small content of chromophore cation and also depend on the calcination temperature.

A distinct example [8] is that of the non-calcinated pink pigments, with the  $\text{CoAlO}_x$  chemical formula, that have brightness values from 35.0 and 40.0, while those with the  $\text{ZnCoAlO}_x$  formula have higher values (between 41.0 and 44.0), corresponding to the blue-green range. In both cases the brightness values are rather high. Moreover, after a thermal treatment at temperatures of over 1200°C, the  $\text{CoAlO}_x$  pigments have a reduced brightness, between 40 and 7.0, independent of their chemical composition, while those with the  $\text{ZnCoAlO}_x$  formula have a smaller brightness, compared to the non-calcinated samples (between 6.0

and 17.0). Therefore, researchers came to the conclusion that sample brightness decreases as cobalt content and calcination temperature rise. Moreover, in accordance with the Temperature-programmed reduction (TPR) results, considering the less intense, octahedral coordinated, pink pigments, that have Co(II) based structural elements and admitting that they could exist both as Co(II) and as Co(III), researchers pointed out that these pigments will have a darker colour.

The same study [8] mentions that the alterations noticed in the chromatic scale of these pigments depend on the values of  $a^*$  and  $b^*$  parameters and the molar ratio of the component cations. The non-calcinated samples of those pigments have rather high values of  $a^*$ , which corresponds to a more reddish colour. The values of  $a^*$  and  $b^*$  parameters for pigments that have only Zn(II) are very similar, while for the  $b^*$  parameter a rise in value is registered, as the cobalt content drops. After calcination of the pigments, for  $a^*$  and  $b^*$  pair, values closer to pink were registered for the  $\text{CoAlO}_x$  type pigments, shifting to dark blue. For the  $\text{ZnCoAlO}_x$  type, the shift was from green-blue to dark green. Therefore, the calcinated  $\text{CoAlO}_x$  type pigments have negative values for  $a^*$  (green) and  $b^*$  (blue), while the  $\text{ZnCoAlO}_x$  samples have positive values for the  $b^*$  parameter. In the case of the aluminium rich samples ( $x = 2$ ), the  $L^*$  and  $a^*$  values rise as the aluminium level rises, while the  $b^*$  parameter drops heavily towards more negative values. No effect has been noticed on colour, when altering the Zn(II) concentration in the aluminate. In the case of the  $\text{Zn}_{1-x}\text{Co}_x\text{Al}_2\text{O}_4$  pigments, whose brightness should vary according to their molar ratio,  $\text{Co(II,III)/Zn(II)} = (x+y)/(1-x-y)$  and their calcination temperature, researchers found that the presence of the tetrahedral spinels inserted between the octahedral structures of Co(II,III), obtained with the migration of Co(II) species from the octahedral structures to the tetrahedral ones, lead to a lower brightness.

In a similar way, for the ceramic pigment with the  $\text{Mg}_{0.5}\text{Co}_{0.5}\text{Al}_2\text{O}_3$  formula [9], based on the values of  $a^*$  (4.0557) and  $b^*$  (-26.6345), the authors suggest that a colour from the blue-reddish range is associated with the existence of Co(II), octahedrally coordinated in a *chrysolite* structure, together with Co(II) tetrahedrally coordinated in a *spinel-type* structure. On the other hand, the chemical formula  $\text{Zn}_{0.5}\text{Co}_{0.5}\text{Al}_2\text{O}_4$ , that only has Co(II) tetrahedrally coordinated, registers negative values (-3.4620, respectively -25.5469) for  $a^*$  and  $b^*$ , indicating the presence of a colour from the blue-green range, associated with the existence of tetrahedrally coordinated Co(II). The brightness of the first pigment is lower ( $L^* = 28.6162$ ) than that of the second pigment ( $L^* = 41.8562$ ).

The analysis for Zn(II), Bi(III) and/or Sb(III) oxyhydroxides 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 [10, 11].

The pigments synthesized in [12], with the same composition as  $\text{ZnCoAlO}_x$ , but burnt at 900°C, have for the  $L^*$  a wide range of values and for  $a^*$  and  $b^*$  values close to 5.0 and -14.0, respectively. The sample has a colour between green and blue, but closer to blue. In a similar way the authors appreciated that ceramic pigments that contain Co(II) and Al(III) are coloured according to the concentration of the Zn(II) cation and not to the molar

percentage of the Co(II) chromophore cation compared to the Al(III) one. The synthesized samples are less luminous than those analyzed in previous studies.

Similarly [13], the colorimetric parameters of the synthesized pigment with the  $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$  formula have values within the ranges: 67.60-70.30 for  $L^*$ , 4.90-8.90 for  $a^*$  and 8.20-19.90 for  $b^*$ . The values were compared with those of some reference, standard, pink pigments used in the ceramic industry. According to the colorimetric analysis, the presence of ZnO in the pigment favours a pink colour. That indicates that responsible for the appearance of the pink colour is the development of a spinel based on zinc and aluminium oxide, doped with chrome. It is true that the appearance of a structure causing a pink coloration corresponds to a pink ceramic pigment with the  $\text{Zn}(\text{Al,Cr})_2\text{O}_4$  formula.

In another study [14], to establish the influence of the molar ration of Cr(VI) doping on the resulting colour, without diminishing the pigment properties, pigments with the  $\text{Al}_{1.55}\text{Cr}_{0.45}\text{O}_3$  (78% mol  $\text{Al}_2\text{O}_3$  - 22% mol  $\text{Cr}_2\text{O}_3$ ) stoichiometry were synthesized, corresponding to the colour range between green and red.

The  $L^* a^* b^*$  colour parameters for orange [15] rutile-based pigments ( $\text{TiO}_2$ ), are similar for all samples ( $L^* = 76.0 - 77.0$ ,  $a^* = 12.0 - 13.0$ ), except for the rose madder pigment ( $L^* = 80.0$  and  $a^* = 10.0$ ). When those pigments get stabilized thermally by burning them at  $500^\circ\text{C}$ , their brightness is enhanced ( $L^* = 71.0 - 75.0$ ) and shifts to a shade of red ( $a^* = 13.0 - 14.0$ ). In a similar way, the colour of the titanate based brown pigments, doped with Cr, or the rutile doped with Ti, Nb,  $\text{MnO}_2$ , was evaluated by measuring the  $L^* a^* b^*$  colorimetric parameters with positive values, which vary as follows:  $L^*$  can be found in the 52,70 - 54,70 range,  $a^*$  in 8,30 - 3,10 and  $b^*$  in the 11,40 - 7,00 range, corresponding to the red-yellow field [16,17].

A pigment very similar to those synthesized by our team, corresponding to the  $2\text{PbCrO}_4 \cdot \text{ZnCrO}_4 \cdot \text{Zn}_3(\text{PO}_4)_2$  stoichiometry, has an elevated brightness (80.54) and the  $a^*$  and  $b^*$  parameters have positive values (16.14, respectively 82.63), which indicates a colour from the red-yellow range [16].

In the present study two techniques were used to select from the 18 newly synthesized pigments, which were divided into two groups, the ones that can be applied for fritted systems and those for water and oil based paints, based on their thermal and photochemical stability.

## Experimental part

### Materials and methods

The 18 newly synthesized pigments have in common the Zn(II) cation and the  $\text{PO}_4^{3-}$  and  $\text{CrO}_4^{2-}$  anions (or  $\text{Cr}_2\text{O}_7^{2-}$ ) and were grouped in 7 classes, according to their chromophore cations (Mn(II), Fe(II), Fe(III), Co(II), Ni(II) and Bi(III)) used in their synthesis:

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

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

**Group III**, 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  $\text{pH} = 8.0$ , the second at  $\text{pH} = 9.5$  with the chromophore anions:  $\text{CrO}_4^{2-}$  and  $\text{PO}_4^{3-}$ ) and **P8** (synthesized in a neutral medium, at  $\text{pH} = 7.0$ , with the chromophore anion:  $\text{PO}_4^{3-}$ );

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

**Group V**, 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  $\text{pH} = 7.0$ , with the chromophore anion:  $\text{PO}_4^{3-}$  and the second, synthesized in an alkaline medium, at  $\text{pH} = 9.5$ , with the chromophore anions:  $\text{CrO}_4^{2-}$  and  $\text{PO}_4^{3-}$ );

**Group VI**, 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  $\text{pH} = 8.5$ , the second, without the Zn(II) cation, only with Ni(II), at  $\text{pH} = 9.5$  with the chromophore anions:  $\text{CrO}_4^{2-}$  and  $\text{PO}_4^{3-}$ ) and **P16** and **P17** (the first one synthesized in a neutral medium, at  $\text{pH} = 7.0$  and  $6.5$  for the second, with the chromophore anion:  $\text{PO}_4^{3-}$ );

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

The colorimetric measurements were done with a MINOLTA (CM 2002) spectrophotometer that uses light impulses from a xenon-arc lamp with a 0.8 cm in diameter wide opening. The light reflection is axed on a silicon photo diode with wave length measurements between 400 and 700 nm (in 10 nm steps) and  $L^* a^* b^*$  values (Chromatic coordinates: brightness, red/green and yellow/blue).

The analysed samples were first irradiated with an UV lamp at 6, 12 and 18 h, and then thermally treated at  $110^\circ\text{C}$  for 4 h.

For colorimetry the finely ground powder of the newly synthesized pigments, irradiated or thermally treated, and that of the reference sample were spread in a fine layer on ceramic plates and compressed with a spatula before performing colorimetric measurements.

For microscopic analysis we used a Carl-Zeiss optical microscope, *AXIO Imager A1m*, using a 100X magnification in reflection mode with a Dark Field filter (visible examination).

## Results and discussions

The **P1** and **P2** pigments from **Group I** have in common the Zn(II) cation and the  $\text{PO}_4^{3-}$  and  $\text{CrO}_4^{2-}$  anions and were taken during the study as reference samples.

The values of the colorimetric parameters of the 18 newly synthesized pigments are shown in table 1, 2 and 3. Table 1 gives the L, a, b, C and H values after UV irradiation for 6, 12, 18 h while table 2 gives the values of variation of the colorimetric parameters following the irradiation treatment.

The UV irradiation intervals were chosen as such because they only affect the hygroscopic water and the hydric equilibrium of reversible water in a mineral pigment. Those intervals allowed pigment selection for the two groups of applications: for polychrome vitro ceramic materials and for painting materials based on water soluble binders or drying oils.

**Table 1**  
**COLORIMETRIC PARAMETERS VALUES (L\*, a\*, b\*, C\* AND H\*)**  
**FOR THE 18 NEWLY SYNTHESIZED PIGMENTS**

| Samples | Time Irradiation (h) | L*     | a*    | b*     | C*    | H*     |
|---------|----------------------|--------|-------|--------|-------|--------|
| P.1     | Standard             | 84.42  | 10.16 | 42.93  | 44.12 | 76.69  |
|         | 0                    | 84.48  | 10.02 | 43.12  | 44.27 | 76.92  |
|         | 6                    | 85.14  | 10.51 | 41.92  | 43.22 | 75.93  |
|         | 12                   | 81.46  | 9.46  | 40.74  | 41.00 | 76.65  |
|         | 18                   | 81.84  | 10.30 | 38.89  | 42.02 | 75.81  |
|         | t=110°C              | 82.85  | 10.37 | 43.17  | 44.41 | 76.56  |
| P.2     | Standard             | 108.55 | -2.87 | 0.83   | 2.99  | 163.84 |
|         | 0                    | 108.66 | -2.91 | 0.88   | 3.04  | 163.24 |
|         | 6                    | 115.58 | -3.59 | 0.54   | 3.63  | 171.51 |
|         | 12                   | 115.88 | -3.48 | 0.34   | 3.49  | 174.37 |
|         | 18                   | 115.27 | -3.43 | 0.16   | 3.44  | 177.36 |
|         | t=110°C              | 108.60 | -2.88 | 0.84   | 2.99  | 163.82 |
| P.3     | Standard             | 0.00   | 0.00  | 0.00   | 0.00  | 0.00   |
|         | 0                    | 0.00   | 0.00  | 0.00   | 0.00  | 0.00   |
|         | 6                    | 0.00   | 0.00  | 0.00   | 0.00  | 0.00   |
|         | 12                   | 0.00   | 0.00  | 0.00   | 0.00  | 0.00   |
|         | 18                   | 0.00   | 0.00  | 0.00   | 0.00  | 0.00   |
|         | t=110°C              | 0.00   | 0.00  | 0.00   | 0.00  | 0.00   |
| P.4     | Standard             | 0.00   | 0.00  | 0.00   | 0.00  | 0.00   |
|         | 0                    | 0.00   | 0.00  | 0.00   | 0.00  | 0.00   |
|         | 6                    | 0.00   | 0.00  | 0.00   | 0.00  | 0.00   |
|         | 12                   | 0.00   | 0.00  | 0.00   | 0.00  | 0.00   |
|         | 18                   | 0.00   | 0.00  | 0.00   | 0.00  | 0.00   |
|         | t=110°C              | 0.00   | 0.00  | 0.00   | 0.00  | 0.00   |
| P.5     | Standard             | 20.03  | 7.55  | -25.43 | 26.53 | 0.00   |
|         | 0                    | 19.85  | 7.62  | -26.13 | 27.22 | 73.75  |
|         | 6                    | 22.11  | 8.20  | -26.65 | 18.56 | 63.78  |
|         | 12                   | 22.01  | 7.84  | -23.49 | 24.77 | 71.54  |
|         | 18                   | 18.64  | 8.81  | -27.53 | 28.91 | 72.26  |
|         | t=110°C              | 20.06  | 7.53  | -25.56 | 26.47 | 73.32  |
| P.6     | Standard             | 60.31  | 21.60 | 51.73  | 56.06 | 67.34  |
|         | 0                    | 60.43  | 21.41 | 51.80  | 56.05 | 67.54  |
|         | 6                    | 60.53  | 21.75 | 52.13  | 56.49 | 67.36  |
|         | 12                   | 58.22  | 19.92 | 52.38  | 56.15 | 67.26  |
|         | 18                   | 59.66  | 21.64 | 47.54  | 56.67 | 67.55  |
|         | t=110°C              | 60.27  | 21.57 | 51.63  | 55.95 | 67.33  |
| P.7     | Standard             | 53.20  | 16.42 | 46.95  | 49.74 | 70.73  |
|         | 0                    | 53.06  | 16.63 | 47.21  | 50.05 | 70.60  |
|         | 6                    | 53.65  | 16.52 | 47.20  | 50.01 | 70.71  |
|         | 12                   | 53.49  | 16.95 | 46.25  | 49.94 | 70.24  |
|         | 18                   | 53.43  | 16.20 | 45.11  | 50.05 | 69.87  |
|         | t=110°C              | 53.20  | 16.37 | 46.95  | 49.72 | 70.78  |
| P.8     | Standard             | 63.33  | 11.05 | 40.86  | 42.33 | 74.87  |
|         | 0                    | 63.20  | 11.10 | 40.79  | 42.27 | 74.78  |
|         | 6                    | 65.47  | 10.65 | 40.21  | 41.59 | 75.10  |
|         | 12                   | 64.89  | 10.65 | 39.09  | 40.52 | 74.75  |
|         | 18                   | 65.51  | 11.11 | 38.36  | 39.94 | 73.85  |
|         | t=110°C              | 63.65  | 11.06 | 40.69  | 42.17 | 74.81  |
| P.9     | Standard             | 77.72  | 18.22 | 56.56  | 59.42 | 72.14  |
|         | 0                    | 77.98  | 18.26 | 56.78  | 59.64 | 72.17  |
|         | 6                    | 75.73  | 17.27 | 53.36  | 56.28 | 72.07  |
|         | 12                   | 74.89  | 15.33 | 52.73  | 57.08 | 71.84  |
|         | 18                   | 76.67  | 17.82 | 53.29  | 59.69 | 71.70  |
|         | t=110°C              | 77.60  | 18.47 | 56.75  | 59.68 | 71.96  |
| P.10    | Standard             | 75.59  | 17.53 | 53.95  | 56.73 | 72.00  |
|         | 0                    | 75.59  | 17.55 | 54.01  | 56.79 | 72.00  |
|         | 6                    | 76.31  | 17.50 | 54.31  | 57.20 | 72.14  |
|         | 12                   | 76.98  | 16.95 | 52.65  | 55.31 | 72.15  |
|         | 18                   | 76.25  | 17.43 | 51.67  | 54.53 | 71.36  |
|         | t=110°C              | 75.71  | 17.55 | 54.06  | 56.84 | 72.01  |
| P.11    | Standard             | 84.48  | 10.02 | 43.12  | 44.27 | 76.92  |
|         | 0                    | 85.14  | 10.51 | 41.92  | 43.22 | 75.93  |
|         | 6                    | 81.46  | 9.46  | 40.74  | 41.00 | 76.65  |
|         | 12                   | 81.84  | 10.30 | 38.89  | 42.02 | 75.81  |
|         | 18                   | 82.85  | 10.37 | 43.17  | 44.41 | 76.56  |
|         | t=110°C              | 84.48  | 10.02 | 43.12  | 44.27 | 76.92  |
| P.12    | Standard             | 81.94  | 19.43 | -19.37 | 27.44 | 44.90  |
|         | 0                    | 81.99  | 19.31 | 19.48  | 27.43 | 45.24  |
|         | 6                    | 81.90  | 17.68 | -17.13 | 24.62 | 44.09  |
|         | 12                   | 84.09  | 19.37 | -19.34 | 27.37 | 44.96  |
|         | 18                   | 82.14  | 17.89 | -17.42 | 24.97 | 44.24  |
|         | t=110°C              | 82.12  | 19.53 | 19.22  | 27.62 | 44.91  |
| P.13    | Standard             | 88.55  | 11.22 | -4.89  | 12.24 | 336.45 |
|         | 0                    | 88.54  | 11.18 | -4.86  | 12.19 | 336.50 |
|         | 6                    | 88.20  | 11.34 | -5.31  | 12.55 | 334.65 |
|         | 12                   | 88.69  | 11.26 | -5.40  | 12.49 | 334.36 |
|         | 18                   | 89.13  | 11.39 | -5.37  | 12.56 | 335.01 |
|         | t=110°C              | 89.39  | 11.43 | -4.67  | 12.53 | 336.55 |
| P.14    | Standard             | 55.71  | 18.21 | 6.28   | 19.26 | 19.02  |
|         | 0                    | 55.26  | 18.52 | 6.05   | 19.48 | 18.11  |
|         | 6                    | 54.55  | 19.69 | 6.34   | 20.68 | 17.84  |
|         | 12                   | 57.70  | 17.29 | 5.33   | 19.29 | 17.13  |
|         | 18                   | 57.65  | 19.25 | 6.00   | 20.16 | 17.31  |
|         | t=110°C              | 55.91  | 18.28 | 6.32   | 19.34 | 19.01  |
| P.15    | Standard             | 24.79  | 11.01 | 9.27   | 14.40 | 40.10  |
|         | 0                    | 24.71  | 10.76 | 9.06   | 14.47 | 40.09  |
|         | 6                    | 27.66  | 11.17 | 10.73  | 15.49 | 43.84  |
|         | 12                   | 31.04  | 9.86  | 7.57   | 14.43 | 37.50  |
|         | 18                   | 27.74  | 11.24 | 9.75   | 15.48 | 40.96  |
|         | t=110°C              | 24.80  | 11.04 | 9.28   | 14.43 | 40.10  |
| P.16    | Standard             | 55.27  | 19.58 | 5.78   | 20.42 | 16.44  |
|         | 0                    | 55.16  | 19.82 | 5.58   | 20.59 | 15.71  |
|         | 6                    | 56.77  | 19.25 | 5.35   | 19.99 | 15.54  |
|         | 12                   | 57.14  | 18.88 | 5.17   | 19.58 | 15.32  |
|         | 18                   | 58.80  | 18.90 | 4.90   | 19.53 | 14.52  |
|         | t=110°C              | 55.48  | 19.58 | 5.76   | 20.41 | 16.42  |
| P.17    | Standard             | 83.13  | 4.87  | 46.40  | 46.66 | 84.01  |
|         | 0                    | 83.13  | 4.64  | 46.40  | 46.63 | 84.28  |
|         | 6                    | 85.20  | 4.74  | 46.83  | 47.07 | 84.22  |
|         | 12                   | 84.53  | 4.43  | 44.86  | 45.08 | 84.36  |
|         | 18                   | 83.87  | 4.66  | 45.58  | 45.82 | 84.16  |
|         | t=110°C              | 82.92  | 4.94  | 46.81  | 47.07 | 84.02  |
| P.18    | Standard             | 89.30  | 9.30  | 83.09  | 83.61 | 83.61  |
|         | 0                    | 89.32  | 9.29  | 83.03  | 83.55 | 83.61  |
|         | 6                    | 87.15  | 10.32 | 80.53  | 81.18 | 82.70  |
|         | 12                   | 89.39  | 9.02  | 79.90  | 80.41 | 83.56  |
|         | 18                   | 87.71  | 8.88  | 78.48  | 78.98 | 83.50  |
|         | t=110°C              | 89.30  | 9.34  | 83.16  | 83.69 | 83.59  |

Table 3 gives the variations of different colorimetric parameters after a thermal treatment at 110°C for 4 h.

According to the data in table 1, the saturation (C\*) of the P1 pigment drops constantly after each irradiation phase and the tint (H\*) variation gradually intensifies. The values of the L\* (very high), a\* (negative) and b\* (positive) indicate that it has a light yellow-greenish tint within the yellow-green range, but closer to yellow and with a strong brightness.

The P2 pigment from the same group has similar characteristics to P1, except that the light yellow-greenish tint is closer to green, with a tendency to pale.

The fact that the P1 pigment has a colour closer to yellow and the P1 to green, is confirmed by the differences in the grading curve of the sample powders as shown by

the microscopic images in figure 1. The powders of the P2 pigment are much finer than those of P1.

Figure 2 presents the colour variations according to the irradiation time for the P1 and P2 pigments

The P3 and P4 pigments, which are black, have very low values of their colorimetric parameters (most of them registered 0.00), and the nuance variation, saturation and brightness are difficult to assess.

On the other hand, the P5 pigment, from the same group as P3 and P4, has a negative brightness ( $\Delta L^* < 0$ ) in initial state, indicating that it is darker in colour than the reference sample (standard) and the saturation is bigger than that of the referene ( $\Delta C^* > 0$ ). Its crimson colour is in the blue-red range, but closer to blue, with positive values for a\* and b\*.

The fact that the P5 pigment is closer, as colour, to blue is confirmed by the grading curve from the microscopic

**Table 2**  
 VARIATIONS OF THE COLORIMETRIC PARAMETERS ( $\Delta L^*$ ,  $\Delta a^*$ ,  $\Delta b^*$ ,  $\Delta C^*$ ,  $\Delta H^*$ ,  $\Delta E^*$ )  
 AFTER UV IRRADIATION FOR THE 18 NEWLY SYNTHESIZED PIGMENTS

| Samples | Time Irradiation (h) | $\Delta L^*$ | $\Delta a^*$ | $\Delta b^*$ | $\Delta E^*$ | $\Delta C^*$ | $\Delta H^*$ |
|---------|----------------------|--------------|--------------|--------------|--------------|--------------|--------------|
| P.1     | 6                    | 2.63         | 0.01         | -0.59        | 2.70         | -0.58        | 0.17         |
|         | 12                   | 2.34         | 0.13         | -1.47        | 2.76         | -1.45        | 0.20         |
|         | 18                   | 2.66         | 0.27         | -2.44        | 3.62         | -2.44        | 0.28         |
| P.2     | 6                    | 7.03         | -0.72        | -0.29        | 7.07         | 0.64         | 0.39         |
|         | 12                   | 7.33         | -0.61        | -0.49        | 7.37         | 0.50         | 0.58         |
|         | 18                   | 6.72         | -0.56        | -0.67        | 7.67         | 0.45         | 3.67         |
| P.3     | 6                    | 0.00         | 0.00         | 0.00         | 0.00         | 0.00         | 0.00         |
|         | 12                   | 0.00         | 0.00         | 0.00         | 0.00         | 0.00         | 0.00         |
|         | 18                   | 0.00         | 0.00         | 0.00         | 0.00         | 0.00         | 0.00         |
| P.4     | 6                    | 0.00         | 0.00         | 0.00         | 0.00         | 0.00         | 0.00         |
|         | 12                   | 0.00         | 0.00         | 0.00         | 0.00         | 0.00         | 0.00         |
|         | 18                   | 0.00         | 0.00         | 0.00         | 0.00         | 0.00         | 0.00         |
| P.5     | 6                    | 2.08         | 0.65         | -1.22        | 2.59         | -7.97        | 0.56         |
|         | 12                   | 1.98         | 0.29         | 1.94         | 2.79         | -1.76        | 0.87         |
|         | 18                   | -1.39        | 1.26         | -2.10        | 2.81         | 2.38         | 0.56         |
| P.6     | 6                    | 0.22         | 0.15         | 0.83         | 0.87         | 0.43         | 0.43         |
|         | 12                   | -2.09        | -1.68        | 0.65         | 2.76         | 0.09         | 1.80         |
|         | 18                   | -0.65        | 0.04         | 4.19         | 4.24         | 0.61         | 4.14         |
| P.7     | 6                    | 0.45         | 0.10         | 0.25         | 0.52         | 0.27         | 0.00         |
|         | 12                   | 0.29         | 0.53         | -0.70        | 0.92         | 0.20         | 0.85         |
|         | 18                   | 0.27         | -0.22        | -1.84        | 1.87         | 0.31         | 1.82         |
| P.8     | 6                    | 2.14         | -0.40        | -0.65        | 2.24         | -0.74        | -0.33        |
|         | 12                   | 1.56         | -0.40        | -1.77        | 2.39         | -1.81        | 0.00         |
|         | 18                   | 2.18         | 0.06         | -2.50        | 3.32         | -2.39        | 0.75         |
| P.9     | 6                    | -1.99        | -0.95        | -3.20        | 3.89         | -3.14        | 1.14         |
|         | 12                   | -2.83        | -1.57        | -3.83        | 5.01         | -2.34        | 3.40         |
|         | 18                   | -1.05        | 0.40         | -3.27        | 3.46         | -0.13        | -0.13        |
| P.10    | 6                    | 0.72         | -0.03        | 0.36         | 0.80         | 0.33         | 0.10         |
|         | 12                   | 0.80         | -0.58        | -1.30        | 1.99         | -1.42        | 0.10         |
|         | 18                   | 0.66         | -0.10        | -2.28        | 0.62         | -2.20        | 0.62         |
| p.11    | 6                    | 0.72         | 0.35         | -1.01        | 1.29         | -0.90        | 0.57         |
|         | 12                   | -2.96        | -0.70        | -2.19        | 3.75         | -3.12        | -2.10        |
|         | 18                   | -2.58        | 0.14         | -4.04        | 4.80         | -2.10        | 3.50         |
| P.12    | 6                    | -0.04        | -1.75        | 2.24         | 2.84         | -2.82        | 0.33         |
|         | 12                   | 2.15         | -0.06        | 0.03         | 2.15         | -3.07        | -3.07        |
|         | 18                   | 0.20         | -1.54        | 1.95         | 2.49         | -2.47        | 0.24         |
| P.13    | 6                    | -0.35        | -0.35        | -0.42        | 0.56         | 0.31         | 0.30         |
|         | 12                   | 0.14         | 0.04         | -0.51        | 0.53         | 0.25         | 0.45         |
|         | 18                   | 0.58         | 0.17         | -0.48        | 0.77         | 0.32         | 0.39         |
| P.14    | 6                    | -1.16        | 1.48         | 0.06         | 1.88         | 1.42         | 0.40         |
|         | 12                   | 1.99         | -0.92        | -0.95        | 2.39         | 0.03         | 1.32         |
|         | 18                   | 1.94         | 1.04         | -0.28        | 2.22         | 0.90         | 0.60         |
| P.15    | 6                    | 2.87         | 0.16         | 1.46         | 3.22         | 1.09         | 0.97         |
|         | 12                   | 6.25         | -1.15        | -1.63        | 6.56         | 0.03         | 1.99         |
|         | 18                   | 2.95         | 0.23         | 0.48         | 3.01         | 0.48         | 0.36         |
| P.16    | 6                    | 1.50         | -0.33        | -0.43        | 1.60         | -0.44        | 0.35         |
|         | 12                   | 1.87         | -0.70        | -0.61        | 2.09         | -0.84        | 0.40         |
|         | 18                   | 3.53         | -0.68        | -0.88        | 3.70         | -0.89        | 0.66         |
| P.17    | 6                    | 2.07         | -0.13        | 0.43         | 1.12         | 0.41         | 0.22         |
|         | 12                   | 1.40         | -0.44        | -1.54        | 2.13         | -1.58        | -1.70        |
|         | 18                   | 0.74         | -0.21        | -0.82        | 2.12         | -1.08        | -0.69        |
| P.18    | 6                    | -2.15        | 1.02         | -2.56        | 3.11         | -2.43        | -0.92        |
|         | 12                   | 0.09         | -0.28        | -3.19        | 3.20         | -3.20        | 0.00         |
|         | 18                   | -1.59        | -0.42        | -4.61        | 4.90         | -4.63        | 0.20         |

| Samples | $\Delta L^*$ | $\Delta a^*$ | $\Delta b^*$ | $\Delta C^*$ | $\Delta H^*$ | $\Delta E^*$ |
|---------|--------------|--------------|--------------|--------------|--------------|--------------|
| P.1     | 0.31         | 0.00         | 0.13         | 0.12         | -0.03        | 0.34         |
| P.2     | 0.05         | -0.01        | 0.01         | 0.00         | -0.02        | 0.05         |
| P.3     | 0.00         | 0.00         | 0.00         | 0.00         | 0.00         | 0.00         |
| P.4     | 0.00         | 0.00         | 0.00         | 0.00         | 0.00         | 0.00         |
| P.5     | 0.03         | -0.02        | -0.13        | 0.06         | 0.06         | 0.14         |
| P.6     | -0.04        | -0.03        | -0.10        | -0.11        | -0.01        | 0.12         |
| P.7     | 0.00         | -0.05        | 0.00         | -0.02        | 0.05         | 0.05         |
| P.8     | -0.12        | 0.25         | 0.19         | 0.26         | -0.18        | 0.34         |
| P.9     | 0.32         | 0.01         | -0.17        | -0.16        | -0.06        | 0.36         |
| P.10    | 0.12         | 0.02         | 0.11         | 0.11         | 0.01         | 0.17         |
| P.11    | -1.57        | 0.21         | 0.24         | 0.29         | -0.13        | 1.60         |
| P.12    | 0.18         | 0.10         | 0.15         | 0.18         | 0.01         | 0.26         |
| P.13    | 0.84         | 0.21         | -0.22        | 0.29         | 0.10         | 0.89         |
| P.14    | 0.20         | 0.07         | 0.04         | 0.08         | -0.01        | 0.21         |
| P.15    | 0.01         | 0.03         | 0.01         | 0.03         | 0.00         | 0.03         |
| P.16    | 0.21         | 0.00         | -0.02        | -0.01        | -0.02        | 0.21         |
| P.17    | -0.21        | 0.07         | 0.41         | 0.41         | 0.01         | 0.46         |
| P.18    | 0.00         | 0.04         | 0.07         | 0.08         | -0.02        | 0.08         |

**Table 3**  
 VARIATIONS OF THE COLORIMETRIC  
 PARAMETERS ( $\Delta L^*$ ,  $\Delta a^*$ ,  $\Delta b^*$ ,  $\Delta C^*$ ,  $\Delta H^*$ ,  $\Delta E^*$ )  
 AFTER THERMAL TREATMENT FOR THE 18  
 NEWLY SYNTHESIZED PIGMENTS

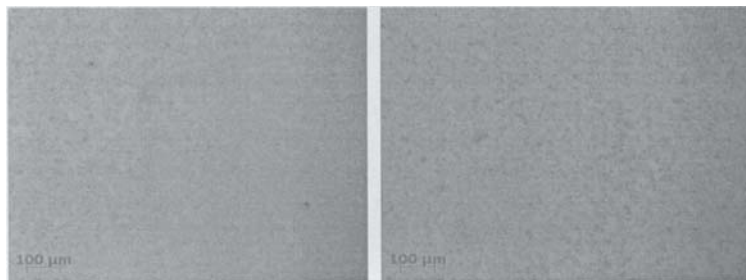


Fig. 1. The microscopic images of the P.1 - a and P.2 - b pigments (Visible light by reflection in dark field, 100X)

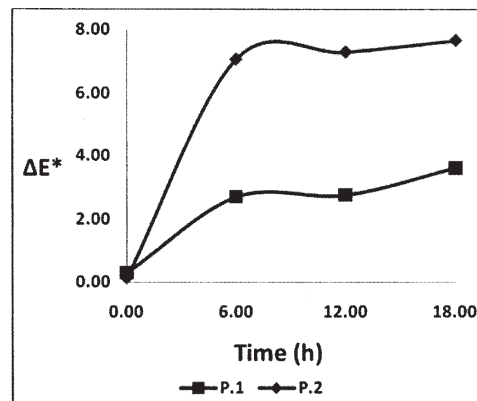


Fig. 2 The colour difference variation based on irradiation time for the P.1 and P.2 pigments

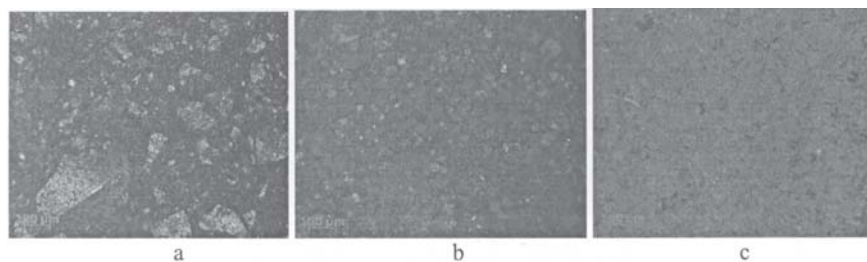


Fig.3. Microscopic images of the P.3 - a, P.4 - b and P.5 - c pigments. (Visible light by reflection in dark field, 100X)

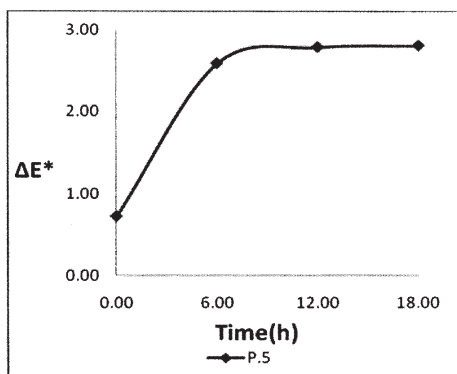


Fig. 4. The colour difference variation according to irradiation time for P.5

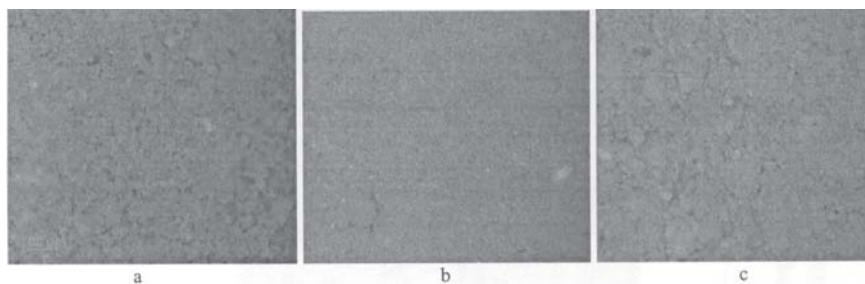


Fig. 5. Microscopic images of the P.6 - a, P.7 - b and P.8 - c pigments. (Visible light by reflection in dark field, 100X)

image of the sample from figure 3-c, which is much lighter for P.3 (coarse grading curve) and P.4 (medium grading curve).

In figure 4 only the colour variation difference, according to the irradiation time, for the P.5 pigment is shown; the P.3 and P.4 pigments have undistinguishable variations.

UV irradiation gradually decreases the brightness and the thermal treatment only slightly decreases it, the effects being difficult to notice. These pigments have a high thermal and photochemical stability.

The brightness of the P.6 pigment in reference state has a positive value ( $\Delta L^* > 0$ ), which indicates the fact that the newly synthesized pigment is lighter in colour (brighter) than the reference sample. This means that its saturation is bigger than that of the reference sample ( $\Delta C^* > 0$ ). The orange colour of the pigment is in the red-yellow range, but closer to red, the  $a^*$  and  $b^*$  parameters having positive values. The P.6 pigment darkens in colour ( $\Delta L^* < 0$ ) after irradiation and thermal treatment.

Nevertheless, the P.7 pigment from the same group as P.6, close in colour and saturation, has in reference state a brightness of negative value ( $\Delta L^* < 0$ ), indicating that it is darker in colour than the master sample and after irradiation and thermal treatment it becomes brighter than the master sample ( $\Delta L^* > 0$ ).

The third pigment from the same group, P.8, of similar orange colour as the other two, has an initial negative

brightness ( $\Delta L^* < 0$ ), being darker in colour than the master sample, the same as P.7. The fact that P.6 and P.8 are close in colour is also explained by the close medium grading curve and P.7, with a very fine grading curve (fig. 5) is, contrary to our expectations, of a slightly lighter tint.

After irradiation and thermal treatment it becomes brighter than the master sample ( $\Delta L^* > 0$ ).

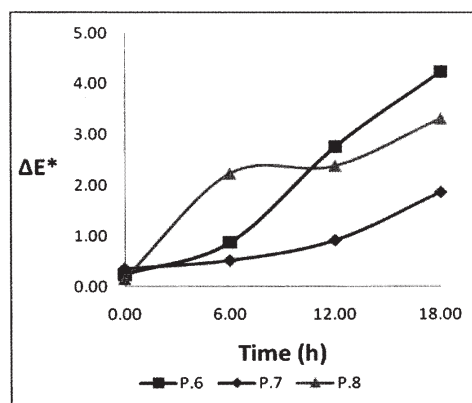


Fig. 6. The variation of colour difference according to time of irradiation for P.6, P.7 and P.8.

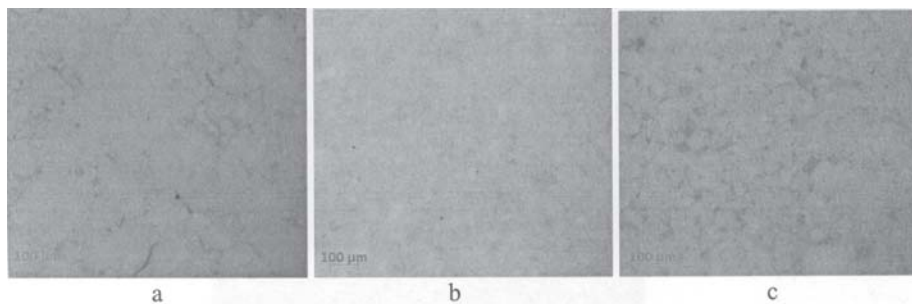


Fig. 7. Microscopic images of the P.9 – a, P.10 – b, P.11 – c pigments (Reflection, 100X DF)

Figure 6 presents the colour difference variations for P.6, P.7 and P.8, according to irradiation time.

The fourth group of pigments, comprised of P.9, P.10 and P.11, is orange to yellow in colour, having the  $a^*$  and  $b^*$  parameters of positive values. The fact that they are closer in colour to yellow, with small shade differences, is confirmed by the grading curve of the sample, as seen in the microscopic images in figure 7.

In reference state they have positive brightness ( $\Delta L^* > 0$ ), indicating that they are lighter in colour (brighter) than the reference sample. At the same time, the colour saturation is higher than that of the reference sample ( $\Delta C^* > 0$ ).

After irradiation and thermal treatment all three samples darken in colour, with a decrease in both brightness ( $\Delta L^* < 0$ ) and saturation ( $\Delta C^* < 0$ ).

Figure 8 presents the colour difference variations of the three pigments, according to irradiation time.

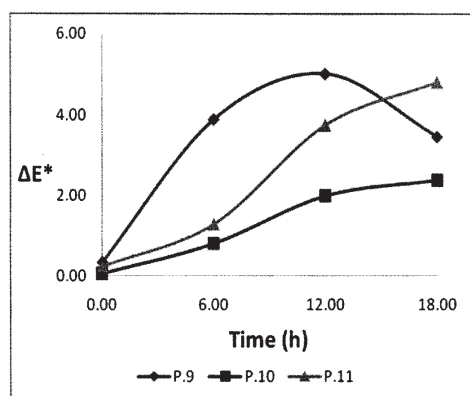


Fig. 8. The colour difference variation according to irradiation time for P.9, P.10 and P.11

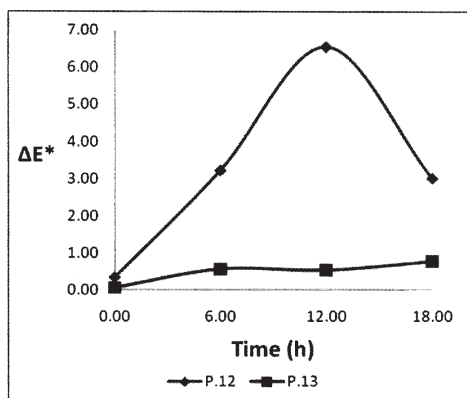


Fig. 10. The colour difference variation according to irradiation time for the P.12 and P.13 pigment

The fifth group, made of two pigments, crimson in colour, shifting towards red (having  $a^* > 0$  and  $b^* < 0$ ), namely P.12 and P.13, with a much higher brightness ( $\Delta L^* > 0$ ), and a lower saturation ( $\Delta C^* < 0$ ) than the reference sample. Figure 9 presents the microscopic images of the two pigments, confirming that their colour similarities have close grading curves.

After UV irradiation and thermal treatment they lighten in colour, compared to the reference sample, registering a positive brightness ( $\Delta L^* > 0$ ), as well as saturation ( $\Delta C^* > 0$ ), which indicates that they become lighter in colour (brighter) than the reference sample.

Figure 10 presents the colour difference variations according to UV irradiation time.

The sixth group consists of four pigments, orange in colour ( $a^*$  and  $b^*$  have positive values), namely: P.14, P.15, P.16 and P.17. They have a low reference brightness ( $\Delta L^* < 0$ ), being darker in colour and with a high saturation ( $\Delta C^* > 0$ ), compared to the reference sample, except for

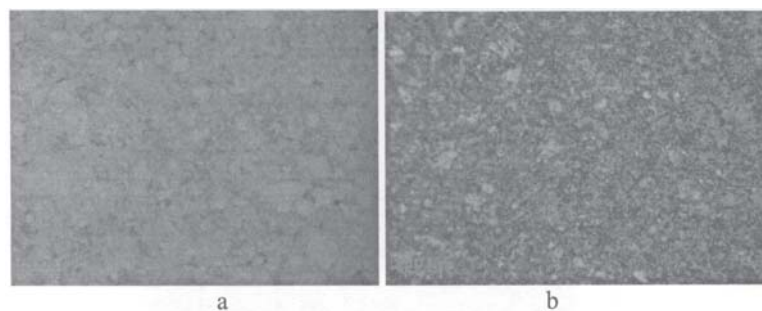


Fig. 9. Microscopic images of P.12 – a and P.13 – b (visible light by reflection in dark field, 100X)

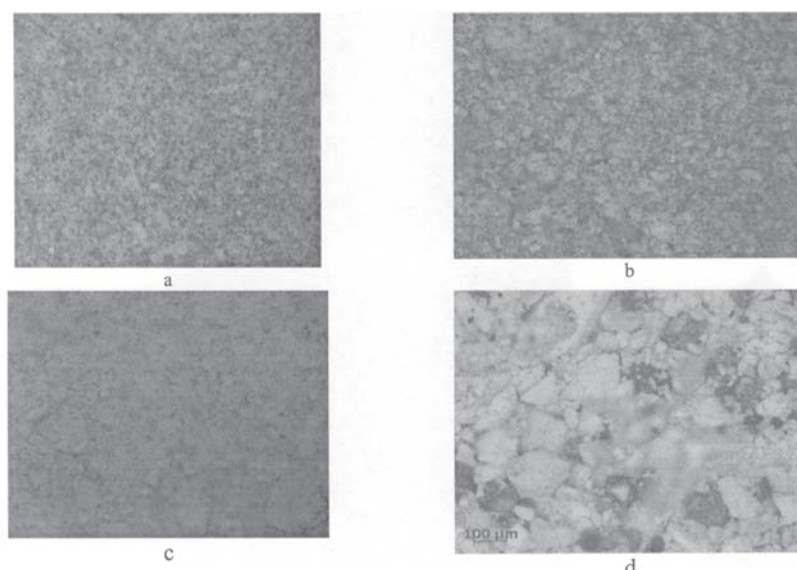


Fig. 11. Microscopic images of the P.14 – a, P.15 – b, P.16 – c and P.17 pigments (visible light by reflection in dark field, 100X)

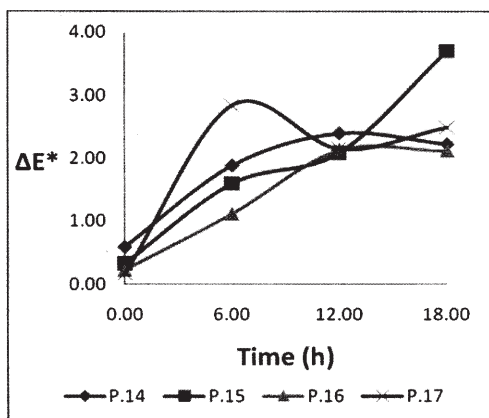


Fig. 12. The colour difference variation according to irradiation time for P.14, P.15, P.16 and P.17

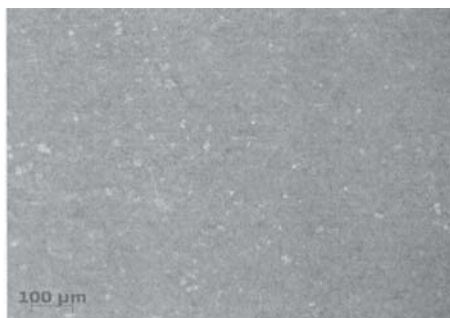


Fig. 13. Microscopic image of the P.18 pigment (visible light by reflection in dark field, 100X)

P.17, which has an initial brightness equal to that of the reference sample and a lower saturation, shifting towards bright yellow, while the others shift towards dark red. The fact that the first three orange pigments (P.14, P.15 and P.17) are closer to red is due to their grading curve, finer than that of P.17, which is closer to yellow and has a coarser grading (fig. 11).

After UV irradiation and thermal treatment the first three pigments (P.14, P.15 and P.16) became lighter in colour (brighter) than the reference sample ( $\Delta L^* > 0$ ) and acquired an intensified saturation ( $\Delta C^* > 0$ ), while the last one (P.17) kept the same brightness but decreased saturation. Figure 12 presents the colour difference variations according to the UV irradiation time for the P.14, P.15, P.16 and P.17 pigments.

The last group, consisting of a single pigment (P.18), yellow, with a slight orange tint, has the initial brightness higher than that of the reference sample ( $\Delta L^* > 0$ ), but a lower saturation ( $\Delta C^* < 0$ ). The fact that the P.18 pigment is closer to yellow can be confirmed by the fine grading curve of the sample, as seen in the microscopic image figure 13.

After UV irradiation and thermal treatment this pigment darkens in colour ( $\Delta C^* < 0$ ) and its saturation is not affected.

Figure 14 presents the colour difference variation according to the irradiation time for the P.18 pigment.

## Conclusions

Based on the experimental data the following conclusion can be drawn:

- P.1 and P.2 pigments are brighter and clearer than the reference sample and remain approximately the same after UV irradiation and thermal treatment. They can be used as fritted pigments for glazed polychrome elements, but also as pigments for oil or water paints;

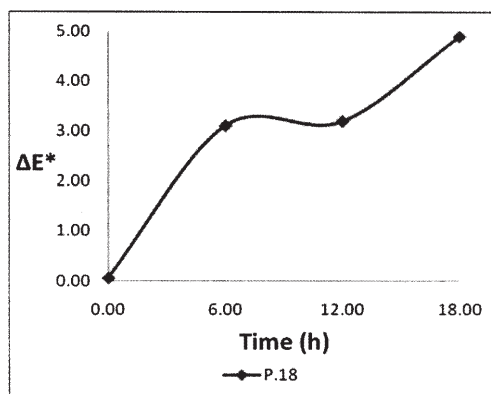


Fig. 14. The colour difference variation according to the irradiation time for the P.18 pigment.

- P.3, P.4 and P.5 pigments are darker, similar to the reference sample. The values of their colorimetric parameters are equal to zero or varying very little and remain unchanged after UV irradiation and thermal treatment. They fit in the same group as P.1 and P.2;

- P.6, P.7 and P.8 pigments are initially lighter and purer than the reference sample, but, after UV irradiation they darken consistently, except for P.7 which, unexpectedly, by having a fine grading curve, is lighter than the reference both after UV irradiation and after thermal treatment. The P.6 and P.8 pigments may only be used for oil or water paints, while P.7 can also be applied for glazed polychrome elements;

- P.9, P.10 and P.11 pigments darken in colour after the UV irradiation and thermal treatment, except for P.9, which lightens. The speed of the process proceeds according to a different rule than that of the other two pigments. All three are recommended for oil or water paints;

- P.12 and P.13 pigments lighten in colour after the UV irradiation and thermal treatment and their saturation enhances as well (P.12 undergoes a discoloration process similar to P.9). Thus they are recommended for application to glazed polychrome elements, but also for oil or water paints;

- P.14, P.15, P.16 and P.17 pigments are initially darker and brighter than the reference sample. After UV irradiation and thermal treatment the first three darken in colour and the fourth lightens (undergoing a discoloration process similar to P.9 and P.12), a fact confirmed by the grading, which is coarse for the last one, making it more thermally and photo-chemically stable. That makes it suitable for glazed polychrome elements and, as with the first three, for oil and water paints;

- The P.18 pigment has a similar behaviour as P.1 and P.2, being suitable for fritted pigments, for glazed polychrome elements, but also for oil and water paints.

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