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FULL PAPER

Influence of the Calcination Temperature on the Colorimetric Properties of Co, Fe and Ni Aluminates in Solid State Reactions Aided by Citrus Pectin

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Abstract:

In the present study, the syntheses of white and colored pigments based on aluminum, citrus pectin, and different coloring ions were performed by using the solid mixture method whit three different calcination temperatures (600 °C, 800 °C, and 1000 °C). The obtained pigments were characterized by colorimetry (CIELAB) and by absorbance and diffuse reflectance spectroscopy (VIS-NIR). All pigments presented different colorations and/or tonalities with increases in the calcination temperature as show in the calculation of the total color difference that indicated differences between all groups of pigments. The increase in the calcination temperature also influenced the values of the colorimetric coordinates and increased the values of the coordinate L* that are related to the percentage of pigment reflectance. This is because higher values of luminosity were obtained for pigments with higher reflectance. Absorbance spectra evidenced the presence of Co^{2+} and Ni^{2+} ions in tetrahedral sites when higher calcination temperatures were applied while Fe^{3+} ions only occupied the octahedral interstices at higher applied temperatures. Generally, Al(pec) and Fe-Al(pec) pigments exhibited higher color stability with increases in the calcination temperature.

Keywords: aluminate; CIELAB (CIE L*a*b*); color; reflectance

1. Introduction

Pigments (from the Latin "pigmentum" - which confers color) [1], are defined as natural or synthetic, organic or inorganic solid particulates, that must be insoluble in the medium in which are applied and should not interact chemically with it [2]. In general, the pigments with industrial application in ceramics, plastics, paints and cosmetics among other sectors, can be described as inorganic substances formed by a host network or matrix, in which the coloring components or chromophores, which usually contain a transition metal or cation [1, 3], are intimately integrated.

Preparation of inorganic pigments has been the focus of several studies [4-7] aiming to obtain new colors and tonalities, or the development of innovative preparation methods that are environmentally more sustainable and with lower costs than the currently used processes. One of the most important class of pigmented materials is based on aluminates, i.e. spinel oxides of the general formula AB_2O_4, where A and B represent divalent and trivalent cations [11-12], since exhibit appropriate chemical and physical properties [13] and depending on the metal ions can be colored, magnetic, and catalytic materials [11-12].Aspects related to the preparation strategy, such as the choice of reagents, synthesis protocols, and calcination temperature can lead to ceramic materials with different colors and properties. For

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example, different shades of blue were obtained in cobalt aluminates prepared by combustion method by Li et al. (2003) [8] simply by varying the calcination temperature, whereas He et al. (2017) [9] developed an innovative one step method for preparation of green and blue cobalt aluminates at the same calcination temperature, varying only the cobalt and aluminum ratio (m/m).

The quality of a pigment is defined by its color and color stability, which are defined by the method of production. An industrial production process always must generate exactly the same final product whenever the same reagents and experimental conditions are employed. One way to carry out color assessment is through the CIELAB colorimetry (CIEL*a*b*) because the visual acuity of human eyes is imprecise and non-reproducible in color determinations or evaluations [10].

The objective of this work was to produce synthetic inorganic pigments by means of a solid mixture method, using citrus pectin. This natural polymer has the advantage of being a low-cost material that already has proven interesting in inorganic syntheses [14] since can be used to generate soft highly porous materials by sol-gel method. We extended the application by demonstrating the possibility of improving the aluminate based ceramic pigments process just by mixing aluminum nitrate nonahydrate and selected hydrated transition metal nitrates, and calcining at different temperatures (600 ºC, 800 ºC, and 1000 ºC). The solid state reaction and densification process lead to the successful formation of highly colored pigments with different tonalities as a function of temperature, that were characterized by colorimetric (CIELAB colorimetry) and spectroscopic (VIS-NIR spectra) methods.

2. Material and Methods

2.1 Materials for pigments synthesis

The inorganic salts: Aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$, 98%), cobalt nitrate hexahydrate ($Co(NO_3)_3 \cdot 6H_2O$, 98%), iron nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$, 98%), and nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, 97%) were purchased from Synth®, and citrus pectin was purchased from Dinamica®. All reagents were used without further purification.

2.2 Synthesis

The pigments were prepared by the solid mixture method, which consists of the physical mixing of the reagents for approximately thirty minutes, or until color homogenization, in a mechanical mixer. Initially, the stock matrix was prepared by the mixture of aluminum nitrate nonahydrate and citrus pectin in the proportion 1:1 (m/m) to obtain a white pigment. To generate three colored pigments, the stock matrix was added transition metal salt (Co, Fe, Ni), in proportion 1:1:0.2 (m/m) respectively. All mixtures were calcined at 600 °C, 800 °C, and 1000 °C (10 °C min^{-1} and compressed air flow) and then pulverized.

2.3 Color and spectroscopy properties study

Diffuse reflectance spectra (VIS-NIR) and absorbance spectra (VISIBLE) were obtained using an Ocean Optics spectrophotometer (USB 2000, Ocean Optics, United State of America), between 400 nm and 900 nm (region of the visible and near-infrared), equipped with a tungsten-halogen lamp and both silicon and germanium detectors. The CIELAB (CIE L*a*b*) colorimetric measurements were performed with a portable colorimeter (CR-400/CR-410 Chroma Meter, Konica Minolta, Japan) under the action of the illuminating D65 source, at a 2° angle. The total color difference among the pigments was evaluated according to the CIE (Commission Internationale de L'Eclairage [International Commission on Illumination - ISO/CIE 11664-6: 2014) [15] using Equation 1. Where Δ is equal to the difference between each color parameter between two pigments and L*, a* and b* are the colorimetric coordinates of the CIELAB space. The L* coordinate varies from black (0) - minimum luminosity to white (100) - maximum luminosity on a grayscale, the coordinate a* varies from red axis (a* positive) to green axis (a* negative) and coordinate b* varies from yellow axis (b* positive) to blue axis (b* negative). The coordinates a* and b* have specific numerical limits ranging from -128 to +128.

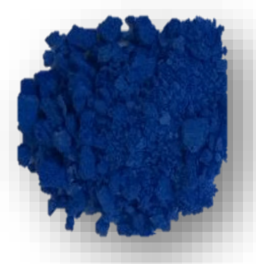
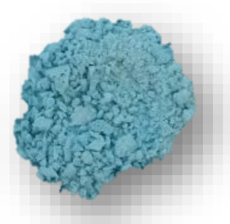
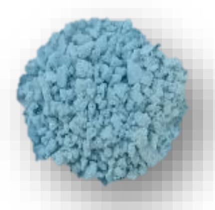
$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

Equation 1. Calculation of total color difference [16].

3. Results and Discussion

Photographs and identification of pigments samples in powder form are shown in Table 1. The data related to the nomenclature and color of each pigment according to the calcination temperature. The $Al_{(pec)}$ pigments showed white coloration independent of the applied calcination temperature, and the same occurred with $Fe\text{-}Al_{(pec)}$ pigments all orange cor. For pigments containing cobalt and nickel the color varied according to the calcination temperature.

Table 1. Digital photos and identification of the pigments samples in the form of powder.

Sample	Temp. (600 °C)	Temp. (800 °C)	Temp. (1000 °C)
$Al_{(pec)}$	 white	 white	 white
$Co\text{-}Al_{(pec)}$	 purple	 blue	 blue
$Fe\text{-}Al_{(pec)}$	 orange	 orange	 orange
$Ni\text{-}Al_{(pec)}$	 green	 blue	 blue

3.1. Colorimetric analysis

The coloration of pigments obtained at

different calcination temperatures was evaluated by the CIELAB colorimetry or the L*a*b* colorimetric parameters. The values of the colorimetric parameters and the values of the total color differences (ΔE) are listed in Table 2. An analysis of the total color difference (ΔE) among four groups of pigments indicated the lowest values for the group of white $Al_{(pec)}$ pigments that did not exhibit color variation with increases in the calcination temperature. The highest values were observed for the Co-$Al_{(pec)}$ and Ni-$Al_{(pec)}$ pigment groups and mainly with respect to the comparisons between temperatures of 600 °C and 800 °C and 600 °C and 1000 °C given that the change in coloration occurred for these pigments at the fore-mentioned temperatures.

According to Quindici (2013) [17], values of the total color difference of 1.5–3.0 in CIELAB units indicate clear differences in the color evaluation between two pigments (distinguishable relative to the human eye). Values 3.0–6.0 suggest very clear differences in color, and values exceeding 6.0 the indicate strong differences. According to the ΔE values obtained for pigments, the values ranged from distinguishable (for $Al_{(pec)}$ pigments calcined at 600 °C and 800 °C) to extremely high differences (in the case of Co-$Al_{(pec)}$ pigments calcined at 600 ºC and 1000 ºC). This indicated that calcination temperature influences the pigment coloration obtained in all the evaluated cases. The analysis of the photographs of the pigments is shown in Figure 1. This suggests that it is possible to verify that the color variations are not clearly perceptible This is because the human eye is typically unable to differentiate between two colors in which ΔE is lower than 2.0–3.0 units CIELAB [18].

Table 2. Colorimetric parameters of calcined pigments at different temperatures.

Pigment	**Colorimetric Coordinates**		
	L*	**a***	**b***
$Al_{(pec)}$ – 600 °C	67.50	-2.27	1.13
$Al_{(pec)}$ – 800 °C	67.50	-0.37	0.06
$Al_{(pec)}$ – 1000 °C	70.71	-0.58	-0.12
ΔE	**2.85 (600 °C/800 °C)**	**4.47 (600 °C/1000 °C)**	**3.22 (800 °C/1000 °C)**
Co-$Al_{(pec)}$ – 600 °C	34,53	-2.03	-0.49
Co-$Al_{(pec)}$ – 800 °C	35,53	7.59	-22.52
Co-$Al_{(pec)}$ – 1000 °C	35.87	7.97	-26.00
ΔE	**24.06 (600 °C/800 °C)**	**27.43 (600 °C/1000 °C)**	**3.52 (800 °C/1000 °C)**
Fe-$Al_{(pec)}$ – 600 °C	51.91	4.04	19.14
Fe-$Al_{(pec)}$ – 800 °C	46.21	7.52	16.51
Fe-$Al_{(pec)}$ – 1000 °C	54.68	6.90	17.96
ΔE	**7.18 (600 °C/800 °C)**	**4.15 (600 °C/1000 °C)**	**8.62 (800 °C/1000 °C)**
Ni -$Al_{(pec)}$ – 600 °C	52.89	-3.13	9.52
Ni -$Al_{(pec)}$ – 800 °C	53.06	-6.27	-10.21
Ni -$Al_{(pec)}$ – 1000 °C	54.55	-3.88	-11.00
ΔE	**21.86 (600 °C/800 °C)**	**21.75 (600 °C/1000 °C)**	**2.93 (800 °C/1000 °C)**

Figure 1 shows the luminosity graph (controlled by the parameter L* that represents the light–dark axis) of the pigments as a function of calcination temperature. As shown in the figure, the parameter exhibits variable values relative to the groups of pigments because luminosity is dependent on the coloration that they present. The highest luminosity value was obtained for $Al_{(pec)}$ pigments due to its white coloration, and the lowest luminosity values were observed in the $Co\text{-}Al_{(pec)}$ group since its coloration is the darkest among all the pigments. With respect to the $Al_{(pec)}$, $Co\text{-}Al_{(pec)}$, and $Ni\text{-}Al_{(pec)}$ pigment groups, a gain in luminosity was observed with increases in the calcination temperature. In the $Fe\text{-}Al_{(pec)}$ group, the luminosity values did not linearly vary with increases in temperature. The highest variations in luminosity values were observed for pigments in the $Fe\text{-}Al_{(pec)}$ group. The decrease in luminosity values may be indicative of the presence of pores in a material and is related to the loss of incident light.

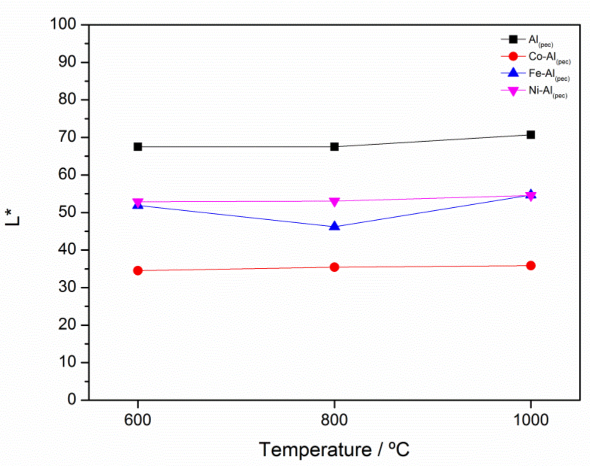


Figure 1. Graphs of luminosity intensity (L *) as a function of temperature and pigment group.

Figure 2 corresponds to a graph that represents the intensity of the green–red color (a* coordinate) as a function of the calcination temperature. More negative values of this parameter indicate a tendency for green coloration and more positive values indicate a tendency for red coloration. With respect to the $Al_{(pec)}$ group, low variations occurred in this coordinate with increases in the calcination temperature. In all the cases, the coordinate assumed negative values and exhibited a tendency to exhibit green color. With respect to the $Co\text{-}Al_{(pec)}$ pigments, increases in temperature generated pigments with a tendency to exhibit red color, and more positive values were obtained with increases in the temperature. With respect to $Fe\text{-}Al_{(pec)}$ pigments, all values of the coordinate a* were positive with a tendency to exhibit red color, and the coordinate a* assumed negative values in all cases with a tendency to exhibit green color with respect to the $Ni\text{-}Al_{(pec)}$ pigments. The highest change related to this coordinate was observed for the $Co\text{-}Al_{(pec)}$ group because the coordinate a* from the quadrant of green color (600 ºC) changed to a red color quadrant (800 ºC and 1000 ºC) when the temperature increased. The change in this coordinate may be responsible for the abrupt change in pigment color from purple (600 °C) to blue (800 °C and 1000 °C).

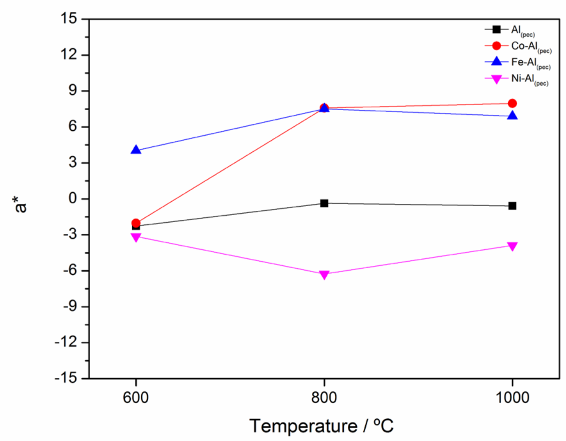


Figure 2. Graphs of the red-green color intensity parameter a* as a function of temperature and pigment group.

The graph (Figure 3) shows the intensity of the yellow–blue color (coordinate b*) as a function of the calcination temperature. With respect to the $Al_{(pec)}$ and $Fe\text{-}Al_{(pec)}$ pigments, small changes occurred in the values of the coordinate although this did not change the pigment color or tonality. With respect to the $Co\text{-}Al_{(pec)}$ pigment, there was an abrupt change in the negative direction of the coordinate (with a tendency to exhibit blue color) with increases in the calcination temperature. With respect to the $Ni\text{-}Al_{(pec)}$ group, there were also changes in the values of this coordinate with increases in the calcination temperature. Additionally, the value obtained was positive at 600 ºC with a tendency to exhibit yellow color. Furthermore, at higher temperatures, the coordinates presented negative values and the tendency to exhibit blue color.

3.2. Diffuse reflectance spectra (VISIBLE-NIR)

Figure 4 shows the diffuse reflectance spectra of pigments in the visible (400–700 nm) and near-infrared (700–900 nm) regions. In the case of all pigments, the analysis indicated that an increase in the luminosity value increased the percentage of reflectance presented by the pigments. The highest reflectance values in the visible region were obtained for all pigments calcined at 1000 °C.

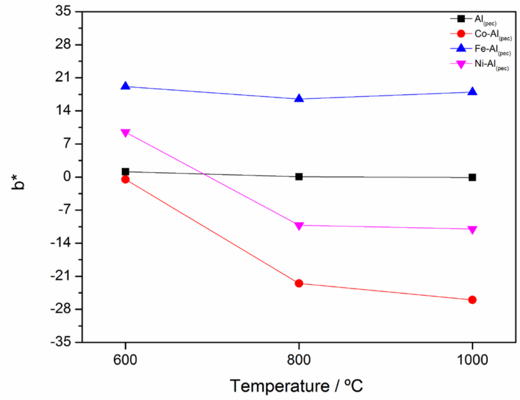


Figure 3. Plots of the yellow-blue color intensity parameter b* as a function of temperature and pigment group.

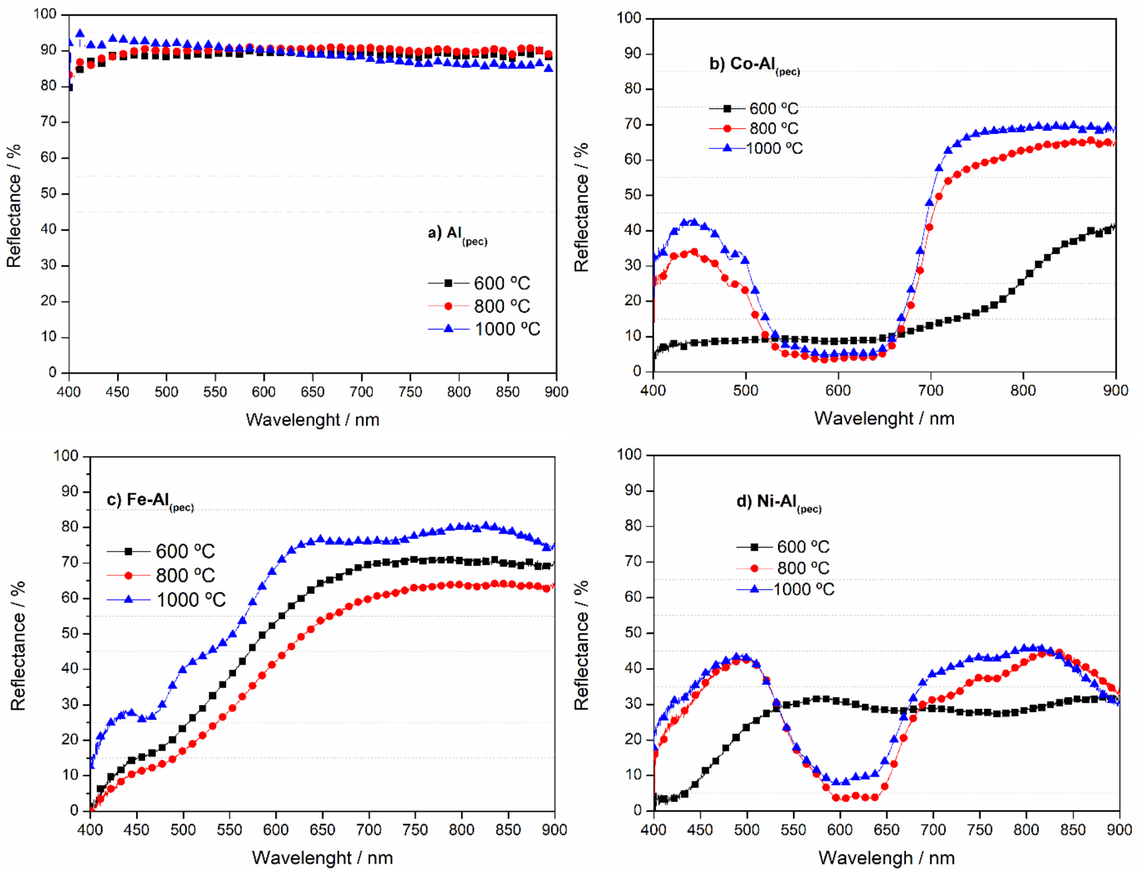


Figure 4. Diffuse reflectance spectra (VIS-NIR) of pigments: a) $Al_{(pec)}$; b) $Co\text{-}Al_{(pec)}$; c) $Fe\text{-}Al_{(pec)}$; and d) $Ni\text{-}Al_{(pec)}$.

With respect to the $Al_{(pec)}$ group of pigments (Figure 4.a), the reflectance spectra (region of the visible) did not present any main band due to the white coloration of the pigments that reflects all the colors of the spectrum and exhibits similar reflectance values in the NIR region. However, only pigments calcined at 600 ºC and 800 ºC displayed a constant percentage of reflectance within this range. The $Co\text{-}Al_{(pec)}$ pigments (Figure 4.b) calcined at 800 °C and 1000 °C exhibited a higher percentage of reflectance in the blue region (430 – 485 nm) indicating the blue coloration of these pigments. Nevertheless, reflectance also exists in the green region (485 – 570 nm) albeit in a lower amount, thereby indicating the coexistence of octahedral and tetrahedral sites in the pigment structure [1]. The pigment calcined at 600 °C exhibited the highest reflectance in the green region (485 – 570 nm) and red region (610 – 700 nm) and displayed a purple coloration. This could be related to the presence of secondary or not stable phases of aluminum oxide [1]. The analysis of the percentage of reflectance in the near infrared region for the Co-Al$_{(pec)}$ group revealed that the highest percentages were obtained for the calcined pigments at the highest temperatures with a higher stability of the reflectance curve for these pigments. This is because the reflectance value is considerably lower at 600 ºC, and thus curve stabilization does not occur.

The Fe-Al$_{(pec)}$ group (Figure 4.c) exhibited higher reflectance in the orange region (570 – 610 nm) and red region (610 – 700 nm) illustrating the characteristic of orange color these pigments. Furthermore, constant values of reflectance were obtained in the NIR region with higher percentages for pigments calcined at 1000 ºC and 800 ºC. The Ni-Al$_{(pec)}$ pigments (Figure 4.d) exhibited higher reflectance in the blue region when calcined at 800 °C and 1000 °C and in the green region when calcined at 600 °C. With respect to reflectance in the NIR region, none of the pigments were observed as constant in the examined region. The highest percentages were obtained for the calcined pigments at the highest temperatures ranging to 825 nm because Ni-Al$_{(pec)}$ pigments in this region at 800 ºC and 1000 ºC displayed a decrease in the percentage of reflectance and corresponded to the value of the pigment calcined at 600 ºC.

3.3. Electronic spectra (VISIBLE)

Figure 5 shows the absorbance curves of the pigments. Absorption bands for the Al$_{(pec)}$ group (Figure 5.a) were not found in this region because the pigments are white and absorbed all the wavelengths of the visible light. With respect to the Co-Al$_{(pec)}$ pigment (Figure 5.b) calcined at 600 °C, a wide absorption band exists between 550 – 650 nm. This is more defined for pigments calcined at 800 °C and 1000 °C because an increase in the calcination temperature increases the number of Co^{2+} ions at tetrahedral sites and is related to the $^4T_1(P) \rightarrow {}^4A_2(F)$ transition due to the formation of the cobalt aluminate as revealed by Jafari and Hassanzadeh-Tabrizi (2014) [19]. The Co-Al$_{(pec)}$ pigments (800 ºC and 1000 ºC) presented bands at 480 nm that are related to the occupation of Co^{2+} ions at octahedral sites, which are attributed to the following transition: $^4T_1(P) \rightarrow {}^4T_1(F)$ [20]. None of the pigments displayed intense bands of absorption between 400 – 500 nm, and this is characterized by the green color that occurs due to the presence of Co^{2+} in octahedral sites. Therefore, the origin of the blue pigment color is related to the occupation of Co^{2+} ions in tetrahedral sites [21].

For three pigments Fe-Al$_{(pec)}$ (Figure 5.c) bands in the region of 460 nm occurred and are related to the presence of Fe^{3+} in octahedral coordination, related to the transition $^6A_1(G) \rightarrow {}^4A_1(G)$, $^4E(G)$ [22]. Fe-Al$_{(pec)}$ (1000 °C) showed two other bands at approximately 550 nm (offset) and 635 nm regarding the transitions $^6A_1(G) \rightarrow {}^4T_2(G)$ and $^6A_1(G) \rightarrow {}^4T_1(G)$ respectively that represents the octahedral coordination of the Fe^{3+} ion [23].

With respect to the Ni-Al$_{(pec)}$ pigments (Figure 5.c) at 800 ºC and 1000 ºC exhibited bands assigned to the $^3T_1 \rightarrow {}^1T_2(G)$ transition at 580 nm [24], the $^3A_2(F) \rightarrow {}^3T_1(F)$ transition at 600 nm [25] and the $^3A_2(F) \rightarrow {}^3T_2(F)$ transition at 637 nm [25], all characteristic of the presence of Ni^{2+} ions in tetrahedral coordination sites [12, 26] responsible for their blue color. Nevertheless, the pigment obtained upon heat treatment at 600 °C exhibited broad and not well defined bands at 580 nm (shifted, T_d) and at 690 nm ($^3A_2(F) \rightarrow {}^3T_1(F)$, O_h) that indicate the presence of Ni^{2+} ions respectively in tetrahedral and octahedral coordination sites [12, 26].

4. Conclusions

In this study, an increase in calcination temperature influenced the tonality of the Al(pec) and Fe-Al(pec) pigments and the coloration of the Co-Al(pec) and Ni-Al(pec) pigments. Colorimetric measurements (CIELab) indicate that the luminosity (L*) was the colorimetric coordinate with smaller alterations relative to increases in the calcination temperature. Additionally, there was a gain in luminosity for all the pigments when this variable increased. The temperature increase led to higher changes in the parameter b* when compared to those in parameter a*. This change was more intense for Co-Al(pec) and Ni-Al(pec) and resulted in the formation of blue pigments. This alteration is related to the occupation of ions in different sites of the spinel structure. The percentages of reflectance (Visible) are associated with the value of the coordinate L* since an increase in the value of the reflectance presented by a pigment increases the value obtained from the luminosity. All pigments exhibited reflectance in the NIR region. Furthermore, the influence of the synthesis temperature was confirmed by the absorbance spectra that indicated (mainly for the Co-Al(pec) and Ni-Al(pec) pigments) a change in the distribution of the coloring ions at tetrahedral and octahedral sites in the spinel network or higher occupation, Fe-Al(pec) case, of octahedral sites.

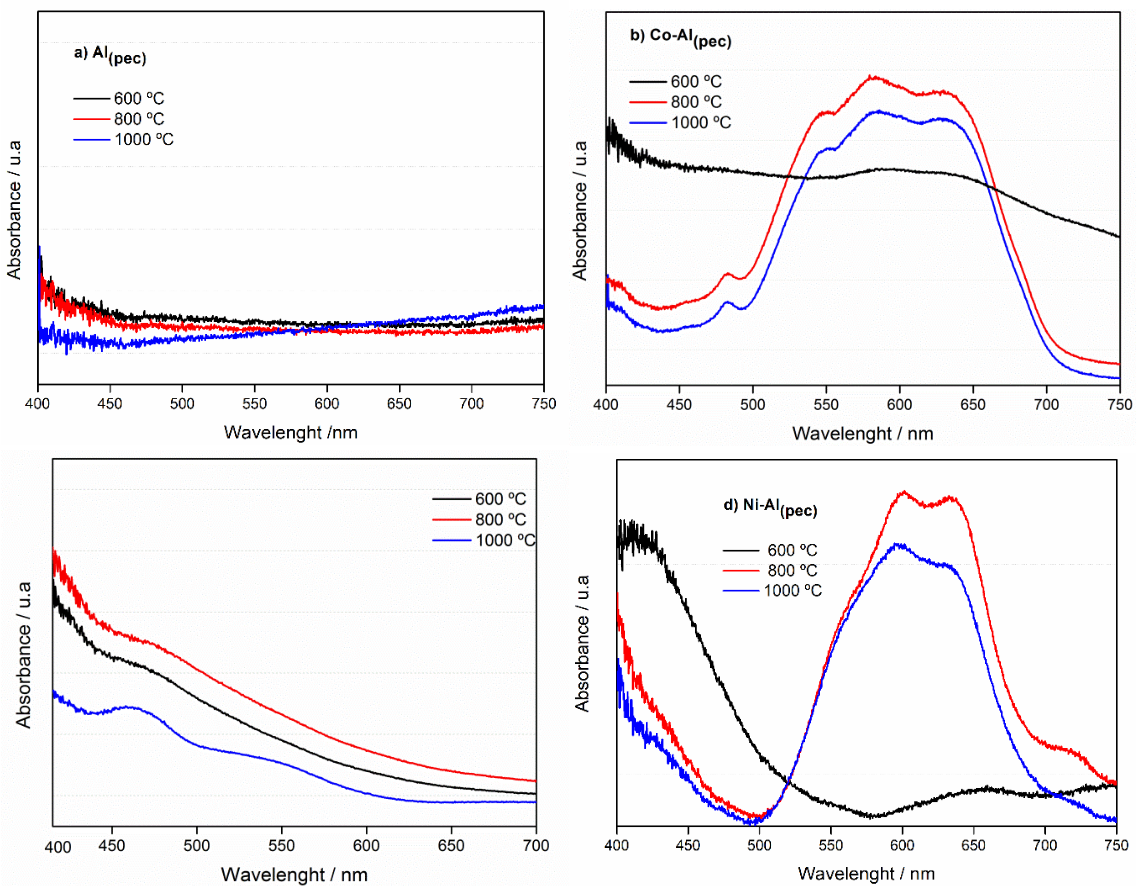


Figure 5. Electronic spectra of the a) $Al_{(pec)}$, b) $Co\text{-}Al_{(pec)}$, c) $Fe\text{-}Al_{(pec)}$, and d) $Ni\text{-}Al_{(pec)}$ pigments, prepared upon heat treatment at 600, 800 and 1000 ºC, in the visible range.

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References and Notes

[1] Costa, A. F.; Pimentel, P. M.; Melo, D. M. A.; Câmara, M. S. C.; Chantelle, L.; Melo, M. A. F.; Medeiros, R. L. B. A. *Cerâmica* **2016**, *62*, 179. [Crossref]

[2] Bondioli, F.; Manfredini, T.; Oliveira, A. P. N. *Ceram. Ind.* **1998**, *13*, 4.

[3] Núñez, I.; Poré, J. V.; Cordoncillo, E.; Escribano, P.; Kozhukharov, V.; Carda, J. B. *Bol. Soc. Esp. Ceram. Vidrio* **1998**, *37*, 291.

[4] Mariani, F. Q.; Borth, K. W.; Müller, M.; Dalpasquale, M.; Anaissi, F. J. *Dyes Pigm.* **2017**, *137*, 403. [Crossref]

[5] Bae, B.; Takeuchi, N.; Tamura, S.; Imanaka, N. *Dyes Pigm.* **2017**, *147*, 523. [Crossref]

[6] Chen, S.; Cai, M.; Ma, X. *J. Alloys Compd.* **2016**, *689*, 36. [Crossref]

[7] Novais, R. M.; Seabra, M. P.; Amaral, J. S.; Pullar, R. C. *Ceram. Int.* **2016**, *42*, 9605. [Crossref]

[8] Li, W.; Li, J.; Guo, J. *J. Eur. Ceram. Soc.* **2003**, *23*, 2289. [Crossref]

[9] He, Y.; Cao, Y.; Liao, H.; Wang, J. *Powder Technol*,

2017, In Press. [Crossref]

[10] McGrath, J. R.; Beck, M.; Hill, M. E. J. *Archaeol. Sci*, **2017**, *14*, 432. https://doi.org/10.1016/j.jasrep.2017.06.020

[11] Gul, I. H.; Maqssod, A.; Naeem, M.; Ashiq, M. N. *J. Alloys Compd*. **2010**, *507*, 201. [Crossref]

[12] Ahmed, I. S.; Dessouki, H. A.; Ali, A. A. *Polyhedron*. **2011,** *30*, 584. [Crossref]

[13] Abaide, E. R.; Anchieta, C. G.; Foletto, V. S.; Reinehr, B.; Nunes, L. F.; Kuhn, R. C.; Mazutti, E. L. F. *Mater. Res. (São Carlos, Braz.)* **2015**, *18*, 1062. [Crossref]

[14] Dalpasquale, M.; Mariani, F. Q.; Müller, M.; Anaissi, F. J. *Dyes Pigm*. **2016**, *125*, 124. [Crossref]

[15] Commission Internationale de L'Eclairage, ISO/CIE Publication 11664-6:2014, Colorimetry – Part 6: CIEDE2000 Colour-Difference Formula. Viena: CIE, 2014.

[16] Francis, F. J.; Clydesdale, F. M. Food colorimetry: theory and applications. 1th ed. Connecticut: AVI Publishing Company, 1975.

[17] Quindici, M. O segredo das cores. 1st ed. São Paulo: All Print, 2013, p. 204.

[18] Mokrzycki, W.; Tatol, M. *Machine Graphics and Vision*. **2011**, *4*, 383.

[19] Jafari, M. Hassanzadeh-Tabrizi, S. A. *Powder Technol*. **2014**, *266*, 236. [Crossref]

[20] Abritta, T.; Blak, F. H. *J. Lumin*. **1991**, *48-49*, 558. [Crossref]

[21] Cava, S.; Tebcherani, S. M.; Pianaro, S. A.; Paskocimas, C. A.; Longo, E.; Varela, J. A. *Mater. Chem. Phys*. **2006**, *97*, 102. [Crossref]

[22] D'Ippolito, V.; Andreozzi, G. B.; Bosi, F.; Halenius, U.; Mantovani, L.; Bersani, D.; Fregola, R. A. *Mineral. Mag*. **2013**, *77*, 2941. [Crossref]

[23] Sherman, D. M.; Waite, D. *Am. Mineral*. **1985**, *70*, 1262.

[24] Lorenzi, G.; Baldi, G.; Di Benedetto, F.; Faso, V.; Lattanzi, P.; Romanelli, M. *J. Eur. Ceram. Soc*. **2006**, *26*, 317. [Crossref]

[25] Vinescu, D.; Papa, F.; Ianculescu, A. C.; Balint, I.; Carp, O. *J. Nanopart. Res*. **2013**, *15*, 1456. [Crossref]

[26] Ragupathi, C.; Vijaya, J. J.; Kennedy, J. L. *J. Saudi Chem. Soc*. **2017**, *21*, 231. [Crossref]