Water-based ink-jet ink based on nano Ni and Sb doped TiO₂ prepared for printing on ceramics

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ABSTRACT
This study reports a simple approach to prepare a nano-TiO₂-Sb-Ni yellow ink-jet ink. Yellow pigments, in terms of their morphology and color appearance, were synthesized by changing Ni/Sb molar ratios and calcination temperatures. Moreover, the particle size of optimal nano-TiO₂-Sb-Ni pigment controlled by CTAB and PVP in a co-precipitation process. TGA, spectrophotometry, and XRD were used to characterize the prepared nano-TiO₂-Sb-Ni pigments. SEM and TEM were used to investigate the morphology and size of the prepared nano-pigments, respectively. Finally, the synthesized spherical nano-pigment had an average diameter of 65 nm was well dispersed in water. A general ink-jet printer printed the stable, homogenous nano-ceramic ink. Ultimately, the more yellow appearance could be obtained through increasing the number of printing runs.

1. Introduction

The drop-on-demand direct ceramic ink-jet printing (DCUP) is an essential developing technology that enables printing on ceramic tiles and glass substrate. Besides ink-jet printing, a variety of processing operations such as stereo-lithography, selective laser sintering, laminated object manufacturing, 3D printing, and dip coating have been used to fabricate ceramic objects [1–6]. The ink-jet printing process has turned to become a leading technology in ceramic tile decoration thanks to its non-contact process, which leaves no patterning, etching, or contamination. However, nozzle clogging caused by various factors such as agglomeration of nanoparticles, wrong pigment size, or physicochemical properties of inks is still a problem associated with ink-jet printing. For this reason, the dispersion stability of the ceramic nano-pigments should be considered in the process of the ink-jet formulation [7–14].

Among different types of ink-jet inks, water-based inks are more environmentally friendly than solvent and oil-based inks, which is why the current project attempts to formulate a water-based ceramic ink-jet ink. The presence of water in ink makes its production process more cost-effective and less polluting.

In ink-jet printing, the quadrichromy process (CMYK: cyan, magenta, yellow and black colors) is employed in the decoration of ceramic tiles. Therefore, each primary

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color ceramic nano pigment should be separately prepared with its appropriate properties to decorate ceramic tiles via ink-jet printing.

To prepare a yellow ceramic nano-pigment, TiO$_2$ was nominated as a base element. Due to its chemical inertness, high chemical stability, photocatalysis, and cost-effectiveness, TiO$_2$ has been widely used in the ceramic industry [15–19]. Some researchers have suggested that by doping of TiO$_2$, can the color of pigment be altered. The Sb, Fe, Nb, and Sn ions were doped in titan structure to obtain Cr-free and lower cost yellow pigment for low-temperature applications [20–25].

In this study, the attempt has been made to prepare yellow ceramic nano-pigment based on the rutile structure of TiO$_2$ doped with Sb and Ni. Various methods such as the sol-gel, Maysel, and Maison’s reverse, hydrothermal, micro-emulsion, co-precipitation, and solo-thermal are used to chemical synthesis. The co-precipitation method is a suitable method for the synthesis of yellow pigment based on nano-TiO$_2$-Sb-Ni. The co-precipitation method is a bottom-up method of synthesis in which the reaction between anion solutions (as including negatively charged ions) and cation solutions (as including positively charged ions) leads to the formation of insoluble compounds in the solvent [26–30].

In this study, the nano-TiO$_2$-Sb-Ni pigments with a rutile structure and suitable physical properties have been prepared by the co-precipitation method. Various TiO$_2$-Sb-Ni pigments by changing Ni/Sb molar ratios (1.50, 1.75, and 2.00), and calcination temperatures (750°C and 900°C) in the absence of surfactants were prepared through the co-precipitation process to obtain the optimum TiO$_2$-Sb-Ni pigment in terms of color, morphology.

The morphology and particle size of the best nano-TiO$_2$-Sb-Ni pigments were controlled by changing the amount of polyvinyl pyrrolidone (PVP) and cetyltrimethylammonium bromide (CTAB). At the same time, the other parameters, such as starting materials, pH value, reaction temperature, and calcination process, were kept constant. Then, optimally synthesized nano-TiO$_2$-Sb-Ni pigments with an average size of 65 nm and yellow color were properly dispersed by polyacrylic acid-co-itaconic acid (AA-co-Al) dispersant in the de-ionized water to prepare the ink-jet ink. Rheology, surface tension, and DLS of the prepared ink are also examined. The print was set to 3 and 5 runs to evaluate variations in the colorimetric characteristics by varying the thickness of the printed film.

The focus of this study was not only to use ink-jet printing technology as an alternative for more conventional methods in the designing of ceramic tiles but also to use water-based ink-jet ink based on a pigment (TiO$_2$-Sb-Ni).

2. Material and methods

2.1. Materials

Titanium (IV) chloride [TiCl$_4$], nickel (II) chloride [NiCl$_2$], antimony trichloride [SbCl$_3$], and cetyltrimethylammonium bromide (CTAB) were obtained from Sigma Aldrich Company. The polyethylene glycol 200, isopropyl alcohol, hydrochloric acid, ammonium solution, and polyvinylpyrrolidone (PVP) were obtained from Merck Company, Germany. All other chemicals used in this work were laboratory-grade, as received from Merck Company, U.K. A fired ceramic wall tile was used as a substrate. The polyacrylic acid-co-itaconic acid (AA-co-Al) as a dispersing agent was synthesized by acrylic/itaconic acid copolymer (2:1) according to the procedure described in references [31].

2.2. Equipment and instrumentation

The crystal structures of nanoparticles were examined with an x-ray diffractometer (XRD) (X’Pert Pro MPD; PANalytical) at a CuK$_\alpha$ radiation to evaluate the mineral composition. XRD pattern was obtained with a step interval of 0.16° between 10°-90° (2θ) at a scanning rate of 0.05° S$^{-1}$ at room temperature. The mass fraction of rutile, $X_{R}$, is determined by equation 1:

$$X_{R} = \frac{1}{1 + 1.26(I_{A}/I_{R})} \times 100$$  \hspace{1cm} (1)

where $I_{A}$ and $I_{R}$ are the intensities of anatase (101) and rutile (110) reflection, respectively.

Thermal behaviors of the formulated ink were analyzed by using a thermogravimeter/differential thermal analyzer (Seiko Exstar 6000, TG/DTA 6100) in the air atmosphere at a heating rate of 10°C/min to report the lowest temperature for burning the organic components out of ink. The Lab jar mill (Iran) consists of a digital controller for changing rotation speed used for ultra-fine grinding and mixing of ceramic ink-jet ink under constant operative rate. Zirconium beads in different sizes (0.2 to 0.7 mm) were used as grinding media. Ceramic tiles were cleaned up on a Bandelin electronic (Germany) Sonorex high power ultrasound bath. The prepared ceramic ink was filtered through a 0.45 µm and 0.2 µm Sartorius filters (Göttingen, Germany) before the printing process. The ink particle size distribution was investigated by dynamic light scattering (DLS) (Zetasizer Nano Z.S., Malvern) instrument. The zeta potentials of optimum pigment (0.10 wt) that suspended in ethanol and de-ionized water at different pH were characterized by an electroacoustic technique (Zetasizer Nano Z.S., Malvern). An Epson Stylus Photo PS50 printer was used to print the prepared ceramic slides. The printed ceramic slides were subsequently dried and heat-treated in an Azar 1250 furnace at different temperatures. The
MiniScan EZ spectrophotometer from Hunter Lab was used to measure the reflectance spectra of samples three times over the visible wavelengths from 400 to 700 nm by 10 nm intervals. Then, the colorimetric attributes of samples over the CIELAB and CIELCH color order systems were computed by using the measured reflectance spectra under the D65 standard illuminant and CIE 1964 standard observer. In the CIELAB color orders system, \( L^* \) indicates the lightness attribute of specimens from the minimum value of (0) for black to the maximum value of (100) for white [32–35]. The \( a^* \) and \( b^* \) parameters represent the hue attribute of samples while the \( a^* \) axis indicates the red (positive \( a^* \) values) and green (negative \( a^* \) values) appearance of samples, and the \( b^* \) axis refers to the yellow (positive \( b^* \)) and blue (negative \( b^* \)) properties. In CIELCH color space as the polar form of Cartesian CIELAB color space, the \( C^* \) and \( h^\circ \) respectively indicate the chroma and the hue angle of objects while the more saturated sample in hue attribute benefits from the higher \( C^* \) parameter [32]. The values of \( pH \), surface tension, and viscosity of the prepared ink were obtained using 827 pH (Metrohm), tensiometer K100MK2 (Kruss), and rheometer MCR 300 (Aton pair) devices, respectively. A scanning electron microscope (SEM) (LEO 1455VP) was used to determine the morphology of the prepared nanoparticles. TEM was used to determine the shape and size of the nano-ink using EM900 (Zeiss). Turbidimeter (TUB) 2100AN (HACH) was employed to evaluate the stability of the prepared ceramic ink.

### 2.3. Preparation of nano-TiO\(_2\)-Sb-Ni pigment

Antimony trichloride \([\text{SbCl}_3]\) (1.92 mMol, 0.44 g) was added drop-wise in chloric acid (10 ml) at 70°C through stirring at 200rpm. Then, nickel (II) chloride \([\text{NiCl}_2]\) with different Ni/Sb molar ratios (1.50, 1.75, and 2.00) was added into the prepared solution to determine the optimum Ni/Sb molar ratio to synthesis optimal nanopigment. Subsequently, titanium (IV) chloride \([\text{TiCl}_4]\) (27.30 mMol, 5.18 g) was added drop-wise to the prepared mixture to obtain a semi-transparent mixture. The mixture stirred for 15 minutes, and then the ammonia was slowly titrated at room temperature until \( pH \) became alkaline (up to \( pH \approx 8 \)) to precipitate antimony hydroxide, nickel hydroxide, and titanium hydroxide. After 3 hours, the resulting precipitation products were separated through a centrifugal separator and then washed more than three times with the de-ionized water and industrial ethanol to remove the impurities. Then, the collected powder dried at 80°C for 24 hours. Finally, the resulting powders were calcinated at 750°C at the rate of 10°C/min for 2 hours. The subsequent pigments were different in terms of color, particle size, and morphology.

### 2.4. Preparation of nano-TiO\(_2\)-Sb-Ni pigments in the presence of CTAB and PVP

The pigments were prepared by the earlier method in the molar concentration ratio of Sb: Ni = 1.75, while the PVP and CTAB were added to the mixture at different concentrations (Table 1) at 70°C through stirring of 200rpm. The mixture stirred for 30 minutes, and then slowly titrated with ammonia at room temperature until \( pH \) became alkaline (up to \( pH \approx 8.0 \)) to precipitate antimony hydroxide, nickel hydroxide, and titanium hydroxide. After 3 hours, the resulting precipitation products were separated through a centrifugal separator and then washed more than three times with the de-ionized water and ethanol to remove the impurities. At that time, the collected powder dried at 80°C for 24 hours. Finally, the resulting powders were calcinated at 750°C at the rate of 10°C/min for 2 hours. The subsequent pigments were different in terms of color, particle size, and morphology.

### 2.5. Preparation of ceramic ink

The ideal synthesized nano-TiO\(_2\)-Sb-Ni pigments (Pigment2 and Pigment15) (10.00 wt%) were formulated with the small amount of poly (AA-co-AI) as a dispersant (2.00 wt%), polyethylene glycol 200 (5.00 wt%), isopropyl alcohol (5.00 wt%) additive (10.00 wt%) and de-ionized water (78.00 wt%). Then, within a ball-milling process, the stable and homogenous nano-inks were obtained as Ink1 and Final ink, respectively. De-ionized water, as the primary solvent, provides green environmental protection and has a low-cost advantage. Finally, rheology, surface tension, and DLS of the prepared ink were evaluated.

| Table 1. Nano-TiO\(_2\)-Sb-Ni pigments in the absence and presence of CTAB and PVP. |
|:----:|:----:|:----:|:----:|:----:|
| **Pigment** | \( \text{Ni: } \text{Sb} \) | \( \text{PVP (wt %)} \) | \( \text{CTAB (wt %)} \) | \( \text{Calcination Temperature (°C)} \) |
| 1 | 1.50 | - | - | 750 |
| 2 | 1.75 | - | - | 750 |
| 3 | 2.00 | - | - | 750 |
| 4 | 1.50 | - | - | 900 |
| 5 | 1.75 | - | - | 900 |
| 6 | 2.00 | - | - | 900 |
| 7 | 1.75 | 0.20 | - | 750 |
| 8 | 1.75 | 0.40 | - | 750 |
| 9 | 1.75 | 0.60 | - | 750 |
| 10 | 1.75 | 0.80 | - | 750 |
| 11 | 1.75 | 1.00 | - | 750 |
| 12 | 1.75 | 1.20 | - | 750 |
| 13 | 1.75 | 0.60 | 0.20 | 750 |
| 14 | 1.75 | 0.60 | 0.40 | 750 |
| 15 | 1.75 | 0.60 | 0.60 | 750 |
| 16 | 1.75 | 0.60 | 0.80 | 750 |
| 17 | 1.75 | 0.60 | 1.00 | 750 |
The compatibility of ink with print-head and the interactions between inks and substrate are essential aspects for good quality printing. Therefore, the physical ink parameters must meet the recommended specification of the print-head. Epson stylus P50 printers use DX5 water-based piezoelectric print-head. Consequently, for good jetting performance without nozzle clogging, the ink formulation was made up of 10.00 wt% pigments.

2.6. Ink-jet printing of nano-ceramic ink

The ceramic substrates were cleaned with isopropanol, acetone, and methanol in an ultrasonic bath, subsequently. Finally, the cleaned ceramic substrates boiled in isopropanol inside an ultrasonic bath. The pH of the ink was fixed to 7.0–7.5 by using a buffer solution to avoid damaging the cartridge and print head.

The Epson stylus P50 printers use the DX5 water-based piezoelectric print-head with a connecting ink cartridge. This type of printer is dominant in graphic, photo quality, and text printing. It has 90 active nozzles, and each nozzle delivers a 1.5 picoliter (1.5*10^{-12} drop). In this study, this printer was used as a lab-photo quality printer. However, the industrial printer has 2000 active nozzles, and each nozzle delivers a 6 picoliter drop up to 160 picoliters. Therefore, the amount of ink printed onto the ceramic tile by the Epson Stylus P50 printer is less than the amount of ink that will be jetted by industrial printer with Xaar 2001 printer-head. Consequently, the prints were set to 3 and 5 runs by a computer program to evaluate the variation in the colorimetric characteristics by changing the thickness of the printed film. After printing, the ink-jet-printed nano-thin films were annealed at 750°C temperature at a rate of 10°C per minute, while total infusing time was 2 h, after which it was cooled down to the room temperature.

3. Results and discussion

3.1. Characterization of nano-TiO2-Sb-Ni pigment

The different synthesized nano-TiO2-Sb-Ni pigments, which were various regarding Ni/Sb molar ratios and calcination temperatures, were characterized based on their color and morphology. The colorimetric specifications of different synthesized nano-TiO2-Sb-Ni pigments (Pigments1 to 6), is presented in Table 2. According to Table 2, the (Pigment2) with the maximum L* and b* values benefits from the highest lightness and yellowness appearance among all other nano-pigments. Besides, the highest C* value, Pigment 2, benefits from the most hue saturation rather than the other synthesized nano-TiO2-Sb-Ni pigments. Meanwhile, the achieved hue angle (h°) of 85.98 proves the closeness to the b* axis, indicating the higher purity of the yellow appearance of Pigment 2.

X-ray diffraction patterns of the synthesized nano-TiO2-Sb-Ni pigments, which were calcinated at various temperatures, 750°C and 900°C, are displayed in Figure 1. Several diffraction peaks are recognized in the patterns. The rutile and anatase phases are identified in both samples according to JCPD card numbers 01-076-0318 and 0-001-0562, respectively. The main phase was rutile in both samples. The transformation of anatase into rutile occurred at 750°C. Therefore, the content of the anatase phase gradually decreased from 27.00 to 15.00 wt. % by the increase in temperature. Accordingly, as the calcination temperature rose from 750°C to 900°C, the percentage of the rutile phase went up. By raising the temperature, the size of the crystals increased, and a very significant transformation of the anatase phase into the rutile phase occurred.

In the synthesis of nano-TiO2-Sb-Ni pigments, the calcination temperature range played a fundamental role in structural changes. At 750°C, the SEM images (Figure 2) showed a high density of fine particles with spherical

| Table 2. The colorimetric characteristics of diverse synthesized nano-TiO2-Sb-Ni pigments over the CIELAB and CIELCH color order systems. |
|-----------------------------------|--------|--------|--------|--------|--------|
| Pigment  | L*     | a*     | b*     | C*     | h°     |
| 1        | 74.68  | 4.00   | 41.98  | 42.17  | 84.56  |
| 2        | 76.89  | 3.18   | 45.40  | 45.40  | 85.98  |
| 3        | 71.65  | 5.25   | 37.53  | 37.89  | 82.04  |
| 4        | 73.28  | 3.95   | 40.65  | 40.84  | 84.45  |
| 5        | 74.29  | 3.07   | 43.76  | 43.87  | 85.99  |
| 6        | 70.06  | 5.14   | 35.43  | 35.80  | 81.75  |
| 7        | 88.89  | -4.72  | 33.68  | 34.01  | 97.98  |
| 8        | 89.07  | -2.30  | 32.43  | 32.51  | 94.06  |
| 9        | 88.84  | -2.74  | 37.74  | 37.84  | 94.15  |
| 10       | 86.07  | -1.24  | 34.23  | 34.25  | 92.07  |
| 11       | 88.03  | -1.56  | 32.99  | 33.03  | 92.71  |

Figure 1. SEM images of synthesized nano-TiO2-Sb-Ni pigments at various calcinated temperatures.
morphology. As the calcination temperature was raised to 900°C, the particle size increased, and the particles change from a slightly spherical morphology into a rod-like morphology of 300 nm. In other words, as the calcination temperature increased to 900°C, both a growth and a morphological change took place in the particles.

Based on the results, the Pigment2 with Ni/Sb molar ratio of (1.75) and calcination temperature of (750°C) with the most appropriate yellow appearance (Table 2) and the best morphological specification was selected for the preparation of ceramic ink.

In order to formulate a stable ink, measuring the zeta potential or particle surface charge of optimum nano-TiO$_2$-Sb-Ni pigment (Pigment2) at different pH is very important. As the results in Figure 3 indicate, by increasing the pH of the solution, the zeta potential became more negative to −25 mV, which is associated with the high degree of repulsion between particles. However, by decreasing the pH to isoelectric point (pH = 5.3), the zeta potential reduced, and the particles encouraged to interact. Alternatively, at pH = 5, the particles possess a positive charge with low zeta potential that is related to the low degree of repulsion between particles. Therefore, the pH = 7.5 to 8.0 is the optimum pH to formulate ink-jet ink as the system is thermodynamically stable.

3.2. Characterization of nano-TiO$_2$-Sb-Ni pigments in the presence of CTAB and PVP

Table 2 shows the colorimetric properties of various nano-TiO$_2$-Sb-Ni pigments with the 0.60 wt % PVP and different CTAB concentrations. According to Table 2, the nano-TiO$_2$-Sb-Ni pigment synthesized in the presence of 0.60 wt% of CTAB and PVP (Pigment15) shows the maximum $b^*$ value with acceptable lightness attribute (L*). Besides, regarding the highest C* value and the hue angle closeness to the $b^*$ axis, Pigment15 yields the highest yellow appearance among all other pigments prepared in the presence of CTAB and PVP.

3.3. Effect of PVP and CTAB on nano-TiO$_2$-Sb-Ni pigments

The particle size of nano-TiO$_2$-Sb-Ni pigment, which was synthesized without adding PVP and CTAB, was measured to be 200 nm. According to the average particle size of synthesized pigments (Figure 4), by increasing the amount of PVP to 0.60 wt%, the particle size changed to 100 nm. It seems that the cationic ions of nano pigment interacted via chemical absorption with lone electron pairs of N or O in the PVP structure.

![Figure 2](image2.png)

**Figure 2.** XRD patterns of synthesized nano-TiO$_2$-Sb-Ni pigments at various calcinated temperatures.

![Figure 3](image3.png)

**Figure 3.** Zeta potential of optimum nano-TiO$_2$-Sb-Ni pigment (Pigment2) at different pH.
Subsequently, the presence of PVP in synthesized nanoparticles may control the growth of the nanoparticles by its steric effect to prevent agglomeration of the nanoparticles. Therefore, as the amount of PVP increased from 0.20 wt% to 0.60 wt%, the particle size decreased from 200 nm to 100 nm, and the morphology altered to the spherical shape. However, as the amount of PVP increased to more than 0.60 wt%, the nanoparticles agglomerated, and the size of pigments increased.

Furthermore, to control the size and shape of the nano-TiO$_2$-Sb-Ni pigments, the nano-TiO$_2$-Sb-Ni pigments were produced in different concentrations of CTAB and constant PVP concentration (0.60 wt %). The results of SEM (Figures 5 and 6) showed that the addition of CTAB affected the size and morphology of the synthesized nanoparticles. As the amount of CTAB increased from 0.26 wt% to 0.60 wt%, the particle size decreased to 65 nm with spherical morphology without any agglomeration. Typically, CTAB with electrondonor on ammonium nitrogen can interact with the nanoparticles. CTAB also can act as a micelle and forms a similar double-layer structure around the nanoparticle, which not only separates the nanoparticles of TiO$_2$-Sb-Ni by electrostatic forces, but also by the steric effect. However, by increasing the CTAB concentration from 0.80 wt% to 1.00 wt%, the agglomeration occurred, and the particle size increased.

From the colorimetric point of view, comparing the results in Table 2 indicates the effect of adding...
surfactants on the yellow appearance of synthesized nano-TiO$_2$-Sb-Ni pigments. According to Table 2, the lightness attribute (L* value) of nano-pigments increases in the presence of PVP and CTAB from the average range of 73.48 to 88.18, approximately. Besides, the a* parameters decrease from positive values to the negative ones leading to significant changes in hue angle ($h^o$<90° changes to $h^o$>90°). In this case, the redness tint effect of yellow nanopigments shifts to the greenness. In other words, the reddish-yellow appearance of synthesized nano-TiO$_2$-Sb-Ni pigments changes to the greenish-yellow in the presence of PVP and CTAB. On the other hand, it was found that by adding PVP and CTAB, the b* parameter of synthesized nano-TiO$_2$-Sb-Ni pigments decreases. It means that the yellow appearance of nano-pigments decrease while the surfactants were being added. However, it is noticeable that the selected nano-TiO$_2$-Sb-Ni pigment synthesized in the presence of PVP and CTAB benefit from the suitable yellow appearance (Pigment15) concerning its b* value.

To sum up this section, the spherical nano-TiO$_2$-Sb-Ni pigment with suitable colorimetric characteristics was synthesized to use in ink formulation.

3.4. Rheological behavior of prepared nano TiO$_2$-Sb-Ni ink

The viscosity of the prepared ink affects the rheological performances, all along with the ink life, from formulation to spreading over the substrate. Therefore, inks with high viscosity could not jet through the capillary nozzles of the printer. However, expressively low viscosity could reduce the inner resistance of the ink, which makes the ink drop effortlessly and produce unpleasant-printed images. Figure 7 shows the variation of viscosities with the shear rate for nano-TiO$_2$-Sb-Ni ceramic ink on a logarithmic scale. The prepared final ink behaves as Newtonian fluids, although the Ink1, which contains the optimum pigment (Pigment2), behaves as shear-thinning fluids. This observation confirmed that the presence of PVP and CTAB during the nano TiO$_2$-Sb-Ni pigments synthesized effect on the size and morphology of the nanoparticle, which caused changes in ink physical properties and provided an ink (Final ink) with improved rheological behavior. Therefore, the Final ink was chosen for further evaluation of the other physical properties.

3.5. The surface tension of prepared final nano-TiO$_2$-Sb-Ni ink

The surface tension of the ink-jet ink affects not only the wettability of the ceramic ink onto the substrate but also the jet-ability of the ink through the capillary tube of the printer nozzle. Water plays as the carrier, and all its physical properties affect the ink’s properties. The existence of poly (AA-co-Al) as a dispersant and isopropyl alcohol in ink formulation contributed to reducing the surface tension. The surface tension of the final ink-jet ink (Final ink) was found to be 32.90 mN m$^{-1}$. The results were within the values of industrial ceramic ink-jet ink [36,37].

3.6. Turbidometry of the final nano-TiO$_2$-Sb-Ni ink

The stability of the prepared final nano TiO$_2$-Sb-Ni ink-jet ink compared to the Ink1 by turbidimeter. Figure 8 shows the turbidity values of the inks obtained at different times. The turbidity value of the final ink is higher than Ink1. This observation confirmed that the Pigment15, which synthesized
in the presence of CTAB and PVP, has spherical morphology with nano-size, which results in stable dispersion with no agglomeration in the ink solution.

### 3.7. DLS of prepared final nano-TiO₂-Sb-Ni ink

The dynamic light scattering method (DLS) was used to determine the size distribution of dispersed nano-TiO₂-Sb-Ni pigment (Pigment15) with a poly (AA-CO-IA) (Final ink). As Figure 9 shows, the DLS of Final ink confirmed that the distribution of pigments was mono-model with one narrow peak. Therefore, the particles of Pigment15 were well dispersed in the ink formulation without agglomerations.

### 3.8. Morphology of final nano-TiO₂-Sb-Ni ink by TEM

Figure 10 shows the TEM image of the final nano-TiO₂-Sb-Ni ink-jet ink (Final ink). This observation confirmed the well-dispersed spherical particles with minimal size variation (50 nm) and no agglomeration in the solution. The PVP and CTAB formed a shell around the surfaces of the particles protecting them against collision. Therefore, they are stable, uniform, and separated in ink.

### 3.9. Ink-jet printed of final nano-TiO₂-Sb-Ni ink

Table 3 and Figure 11 show the colorimetric attributes and the yellow appearance of the nano-yellow ink, which was formulated with Pigment15. The negative values of a* parameter shown in Table 3 indicate the greenish tint effect of yellow appearance in printed inks. On the other hand, according to Table 3, as the number of printed layers increases from 3 to 5, the yellowness attribute (b* value) as well as the Chroma property (C* value) increase, while the lightness parameter (L* value) decreases. It means that a more saturated yellow appearance of printed films can be obtained as the thickness of them increases by the number of printed layers.

### 4. Conclusions

In this study, the various nano-TiO₂-Sb-Ni pigments were synthesized, while the color and morphology controlled by varying the Ni/Sb molar ratios (1.50, 1.75, 2.00) and calcination temperatures (750°C, 900°C). Based on the results, the nano-TiO₂-Sb-Ni pigments with Ni/Sb molar ratio of (1.75) and low calcination temperature of (750°C) were found with the most appropriate yellow
appearance and the best morphological specification. Moreover, the particle size of optimal nano-TiO\textsubscript{2}-Sb-Ni pigment was controlled by changing the concentration of CTAB and PVP. CTAB and PVP materials affected the shape, size, and optical properties of the synthesized nano-pigments. As the amount of PVP and CTAB increased from 0.20 wt\% to 0.60 wt\%, the particle size decreased from 200 nm to 65 nm, and the morphology altered to spherical. On the other hand, the reddish-yellow appearance of synthesized nano-TiO\textsubscript{2}-Sb-Ni pigments changed to the greenish-yellow in the presence of CTAB and PVP.

**Table 3.** The colorimetric characteristics of the printed nano-TiO\textsubscript{2}-Sb-Ni ink.

| Ink   | Number of printing runs | L*   | a*    | b*    | C*   | h°   |
|-------|-------------------------|------|-------|-------|------|------|
| Final | 3                       | 71.43| -2.43 | 20.83 | 20.97| 96.65|
|       | 5                       | 64.85| -2.72 | 21.99 | 22.16| 97.05|

**Figure 10.** TEM image of Final ink.

**Figure 11.** The yellow appearance of the printed Final ink; in 3 and 5 runs.
of PVP and CTAB. Subsequently, the optimal synthesized nano-TiO$_2$-Sb-Ni pigment with a suitable yellow appearance was selected for ceramic ink preparation. Then, the synthesized spherical nano-pigment was well dispersed in water. Finally, the stable water-based yellow nanoceramic ink was printed with a general ink-jet printer. The yellow-printed pattern was obtained at low calcination temperature at 750°C. By increasing the printing runs of images, a more yellow appearance gained.

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