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Producing Ceramic Toner Via Emulsion Aggregation Method Based on $ZrSiO_4$: Pr Ceramic Pigment

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ABSTRACT

Toner is a powder mainly composed of polymer and colorant that are used as ink in electrophotographic printing. Several methods have been employed for producing toner and one of is emulsion aggregation (EA) method. The purpose of this study is to produce ceramic toner based on $ZrSiO_4$: Pr uses emulsion aggregation method and investigate the effect of ceramic pigment synthesis method on the final properties of the toner. For synthesis of zirconium silicate pigment with Praseodymium dopant, two combustion and combinational methods were studied. Ceramic Toner characteristics were analyzed using a spectrophotometer, X-ray diffraction, scanning electron microscopy, particle size analyzer and differential scanning calorimetry. Structural studies show that the pure phase of zirconium silicate can be identified as a pure phase in the toner and toner particle size and particle size distribution is in the appropriate (4-7 µm) range for printing. Thermal analyzes show an appropriate glass transition temperature at around 77 °C. Color specification shows that in spite of a decrees in color characteristics of the ceramic pigment at the manufacturing process of the toner, after application and baking at a temperature of 1000 °C, the color is converted to a suitable yellow intensity range. Prog. Color Colorants Coat. 14 (2021), 113-120© Institute for Color Science and Technology.

1. Introduction

The beauty of a ceramic piece is a complex interplay of form, color, texture and surface decoration. Ceramics has been decorated since the earliest periods using techniques that have become increasingly sophisticated over time [1]. There is now a technology that represents a significant advance in the process of decorating and providing a radical change in many aspects in the design and manufacturing processes. One type of surface decoration is the decal or transfer, which is traditionally produced through direct screen printing. However, direct screen-printed decals require relatively large, expensive equipment and substantial floor space, and dryers and solvents place heavy energy and environmental demands. Additionally, long production runs are generally required to distribute the cost of color separations, sizing, screens, changeovers and other processes over a large number of decals [2].

Recent developments in digital technology use digital images to generate transfers with a unique color

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palette, simply and without the costs and delays associated with the traditional technique of printing systems with silkscreens. A particular benefit of this technique is to allow achievements unit or in small series as promotional items for event advertising. For manufacturers this technique allows a drastic reduction of their stocks and is an attractive proposition. For example, Ink-jet printing has been developed as a non-contact direct-write technology for the decoration of ceramic tiles [3]. Since 2000, the ink-jet printing for the decoration of ceramic tiles has attracted recent attentions. The conventional printing processes used for ceramic tile decoration are flat screen printing in the 1960s, rotary screen printing in the 1970s and flexographic and intaglio printing in the 1990s [4]. It is necessary for the printing with the conventional methods above to contact the printer with ceramic tiles. However, ink-jet printing as a non-contact deposition method can provide a low-cost, high-definition, efficient use of materials and waste elimination process. Also, the contamination is minimized in ink-jet printing [5].

Today, with new ceramic toners and commercially available digital technology, high-quality, continuous-tone decals can be printed easily and quickly. Short runs and even one-offs are economically possible. Using digital decals, custom-decorated products, prototypes and personalized ware can be manufactured at a reasonable cost. On the other word, the key breakthrough in digital decals was the development of ceramic toners designed to work in commercially available laser copiers and printers [6]. These toners are being produced in Germany through a patented process in which selected ceramic colors-i.e., a flux and ceramic pigment mixtures-are melt-mixed in a suitable resin [7].

In ceramic and glass decoration, the substrates need to be subjected to a subsequent thermal treatment at temperatures above 600 °C to remove the organic components of the toner and enable the inorganic component to be integrated into the decorated surface. The quantity of the inorganic pigments contained in the toner particles needs to be as high as possible in order to assure good color saturation once the organic components have been eliminated by firing [1, 7, 8].

The fabrication of ceramic toners by the traditional method is described by other authors [1-5]. Ceramic toner preparation by the traditional method presents a series of drawbacks. The inorganic components, such as the pigments, display a different fracture strength from that of the plastic organic components, leading the particles to fracture at the boundary between the inorganic particles and the polymer matrix during the toner powder generation process. This gives rise to toner particles with irregular shapes, and inorganic particles that are only partly coated by the plastic matrix, which can lead to problems of electrostatic charging and flowability of the particles. In addition, the high specific weight of the ceramic toner makes it very difficult to obtain a narrow particle size distribution by the traditional method. These drawbacks can lead to printing problems, such as white spots in the images. In other industrial sectors, in which organic colorants are used in preparing toners, the above drawbacks have been avoided by introducing alternative synthesis routes [6, 7].

The possibility of introducing a new kind of toner for ceramic printing market associated with the promotion of common toner properties are beneficial features from industrial and academicals point of view, which lead us to produce ceramic toner with emulsion aggregation method. In the series of previous studies, the authors studied the production of black and color [9, 10] toner. In continuation of our works, for the first time, the current study, introduces the EA ceramic toner for electrophotographic printing, which raises a number of challenges.

Herein, the $ZrSiO_4$: Pr pigment with Praseodymium dopant were synthesize with two combustion and combinational methods and were used to prepare monodisperse semi-spherical composite with poly (styrene-co-acrylic acid) by using an eco-friendly method named emulsion aggregation (EA).

2. Experimental

2.1. Materials

The polymer used in this study was a styrene-acrylic resin (R579; ResinFam Co., Iran) which, according to supplier, had a medium pH value, T_g of 51 °C, and mean particle size of 220 nm. A polyethylene emulsion wax (EE 95, Kala Kar Co., Iran). Polyaluminum chloride was used as coagulation agent. All the above mentioned materials were used as received.

2.2. Ceramic pigment synthesize

For synthesis of zirconium silicate pigment with

Praseodymium dopant, two combustion and combinational methods were studied. Praseodymium oxide (Pr_6O_{11}) is insoluble in water. Therefore, the dissolution rate of this oxide in chloride, sulfuric and nitric acids was investigated first. On the basis of this, 0.1 grams of praseodymium oxide was poured into the acids mentioned. This oxide is in black color. This oxide is deposited in nitric acid and sulfuric acid in a pinkish form, which is not suitable for synthesis and does not actually function in the structure of the doped base. But acid chloride solves this oxide. The color of the solution changes to dark blue at 100 °C after complete dissolution [11, 12].

2.2.1. Combustion method

All used martials is obtained from Merck Co. Two types of urea and citric acid were used to improve the conditions and the type of fuel used on the color properties of the pigment. Also, in synthesis of each sample, two sources of Praseodymium nitrate and Praseodymium solution in HCl were used. Accordingly, by using stoichiometric ratios, 1 g of zirconium nitrate in 20 mL of deionized water was dissolved. Then, the samples were separately added to the fuel of urea or citric acid. Two specimens were also synthesized with Praseodymium solution in HCl in each sample. Two samples were synthesized using nitrate sources with different fuels. The amount of dopant was one tenth of gram and two tenths of gram, respectively.

After dissolving zirconium nitrate in deionized water and adding doping, half a centimeter of tetraetrocyclate solution plus 10 mL ethanol was added to the samples. At this stage, a sample of urea fuel and another citric acid were added. All specimens were evaporated at 80 °C to form white gels. These gels were transferred to a microwave oven and placed under a wavelength of microwave radiation for 5 minutes. Some specimens were heated at 1100 °C for one hour to form a dopant in the structure. The resulting product was porous yellow foam.

2.2.2. Combinational methods

In this method, the fuel discussed in the combustion method was deleted. Zirconium nitrate with 50 mL Tetraethyl orthosilicate and 10 mL ethanol were dissolved in 100 mL of deionized water. These values were all in stoichiometric ratios, and were synthesized in the same manner as the previous one with two doped nitrate Praseodymium and HCl-soluble oxides. All specimens were heated at 80 °C. The ammonia solution was then added to all samples to obtain a white deposit and at 1100 °C for one hour was heated to form a yellow color.

2.3. Ceramic toner production procedure

Ceramic toner was produced via a stepwise procedure, in accordance with previous work [13]. First (step *a*), a 1-liter beaker was filled with 24.5 g styrene-acrylic latex, 2 g ceramic toner, 3 g wax, and 120 g deionized water; then the contents were mixed manually at room temperature for about 15 min. In step *b*, the resulting suspension obtained in *a* mixed using a Homogenizer for 5 min. Next step, that is c, was started by continuous mixing of ingredients at room temperature for about 1 h followed by the addition of a solution of 0.6 g coagulation agent in nitric acid, and were mixed again over 10 min until the pH value of the mixture reached 2. In this manner, a gel was seen to be formed, as a consequence of changing the viscoelastic nature of the suspension from a Newtonian water-like fluid to a shear thinning paste-like gel. In step *d*, the temperature of the mixture was raised to 50 °C for about 30 min while the gel was continually mixed. The mixture was held at this temperature for another 60 min in step *e*, where the temperature of the mixture was increased to 96 °C for 30 min. The last step, denoted as *g*, was started by holding the product of step *f*, at 96 °C for a further 60 min. The ultimate mixture was neutralized with sodium hydroxide solution and cooled down to 25 °C, after which the produced microparticles were isolated from the water, washed to remove divalent ions, filtered, and dried with a frizzed dryer.

To confirm the printability of the produced toner, the resultant toner were printed in a controlled environment [23°C, 50% relative humidity (RH)] using a monochrome laser-jet printer (HP 1100, Laser-jet printer) on the Decal paper. This printer was changed to only have a hot roll fusing system. After application toner was baking at a temperature of 1000 °C.

2.3. Characterization of ceramic toner

X-ray diffraction (XRD) analyses of powder toners are performed on Cu-Kα (λ=1.54056 A°) radiation in diffraction angle (2θ) range of 10° to 100° with a

typical step size of 0.026° by an X-ray diffractometer (STOE Stadi P, Germany) using X'Pert High Score software.

Scanning electron microscopy (SEM S360, Cambridge Instruments Ltd., UK) was, also, conducted to investigate the existence and distribution of nanoAg. The EDX measurements were conducted by using primary electron beam with an acceleration voltage of 20 kV to detect Ag.

Color measurement of the printed toner was conducted on a Gretag Macbeth Color Eye 7000A spectrophotometer (USA). The spectral reflectance factor of all samples was determined and then transformed into CIELAB colorimetric coordinates (L*, a* and b*) using CIE standard illuminant D65 and a CIE 1964 standard colorimetric observer. It is well-known that an increase in the L* indicates the higher lightness of the sample. The a* axis in colorimetric coordinate is green at one extremity (-a*) and red at the other (+a*), while b* axis has blue and yellow extremes, respectively. Therefore, a positive Δa* signifies a color shift toward red, while a negative Δa* feature a color shift toward green. Likewise, a positive Δb* signifies a color shift toward yellow and a negative Δb* indicates a color shift toward blue.

The thermal stability of the samples was determined using a thermogravimetric analyzer (TGA, PerkinElmer USA). The powder toners samples were heated from 25 to 1000 °C with a heating rate of 10 °C min^{-1} under nitrogen atmosphere.

Differential scanning calorimeter (DSC, PerkinElmer USA) was, also, used to investigate thermal properties of the toner. Approximately 5 mg of each powder toner sample was loaded to a pan and sealed with a covering lid. Measurements were conducted over a temperature range of 0-150 °C at a heating rate of 10 °C/min in an atmosphere of nitrogen.

3. Result and Discussion

The first step in the study of structure is provided by the evaluation of X-ray diffraction pattern of sample. All of the synthesized samples are yellow in the two combustion and combinational methods, so it can be assumed that in both methods the zirconium silicate structure is obtained.

Accordingly, the diffraction pattern taken from the combustion sample represents the peaks of this structure without any impurities. In this sample, no impurities such as SiO_2 can be observed, which indicates the complete reaction of the primary precursors based on the stoichiometric amount. This phase, based on the Figure 1, has the highest matching with the JCPDS card number 1367-083-01. The average size of crystalline crystals is about 46 nm using the Sherer method for this sample. Due to the low level of dopant below 5% by weight, there is no evidence of it. The crystalline structure in this tetragonal sample is the dopant placement of praseodymium in its empty spaces.

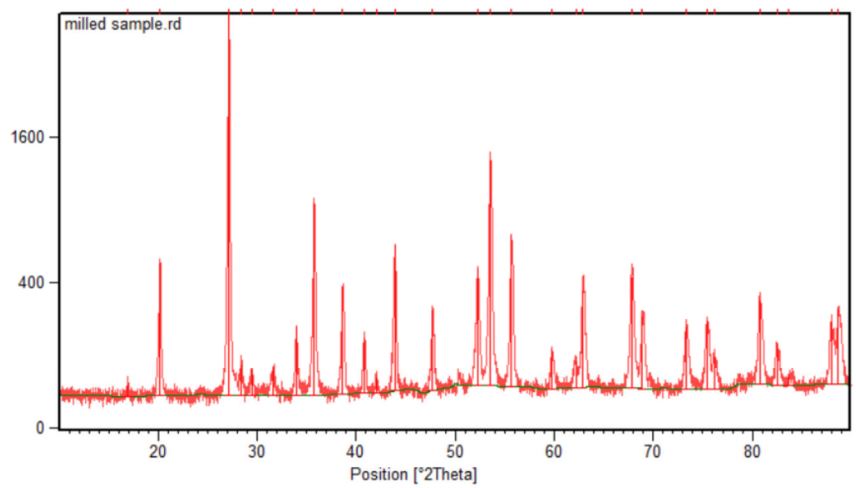

Figure 1: XRD pattern of combustion sample.

The thermal properties of the toner, especially its glass transition temperature (T_g), are of particular importance because of the direct effect that they have on the fusing and toner stabilization of the substrate. When the T_g is low, toner storage conditions are difficult, and when T_g is high, the toner fixation on the substrate is not properly executed, and thus the toner is removed from the surface of the substrate and this causes Printing quality can be severely reduced [14]. Ideal T_g for toner is between 50 and 70 °C [13]. DSC analysis was performed for samples of toner produced under optimum conditions with the aim of determining the T_g. The results show that the T_g for the produced toner is in optimal conditions.

Figure 2 show the TGA results. In all samples, the origin of the degradation is in the range of 200 to 250 °C and the destruction at 400 to 450 °C. This means that there is plenty of time for organic matter to go through the warming up and drying of the glaze and the penetration of the pigment into it. The maximum rate of destruction in these samples is around 400 °C. At a temperature of up to 200 °C, a weight loss trend is observed, which is attributed to the outflow of water and some organic materials. At only 600 °C, only 10% of the original material remains, so that in some instances it is less. This represents a high percentage of organic matter in the toner. Due to the fact that most glazes start to melt at temperatures up to 750 °C, the study of the operation of the glaze is not within the temperature range of this test.

The main polymer decomposition appeared to occur in three phases: the first at about 300 °C, the second before 400 °C, both with important mass losses, and the third in a wider range of temperatures, between 400 and 600 °C. The firing cycles of the samples decorated with this toner would, therefore, need to reach temperatures above 600 °C [6, 7].

The synthesized pigments were characterized by the use of HCl solution containing pradesium ion in two combustion and combinational conditions at the beginning of color synthesis in an aqueous to pink range. After the heat treatment, this color was changed to gray, indicating the absence of doptation of the pradesian ions in the host structure and its oxide formation. The samples synthesized with pradesian nitrate sources as dopant are all yellow. This indicates that dupont is in the host network structure. In two categories, with increasing dopant levels, the intensity and purity of yellow were increased. In a traditional carbon monoxide sample, we are less likely to have a lower brightness than ours. This is due to the high combustion of this fuel with respect to urea and its ability to better break teas at the instant of combustion. For this reason, the dupont is more easily and more in the host network structure. The second one belongs to the urea synthesized sample. This sample has a high bright yellow color. This is due to the extremely low combustion and relative inability to break the TEOS bond. This difference is even evident even after the heat treatment. The reason for this difference in the prudent penetration of pradesium in a solid zirconium silicate structure is at 1100 °C.

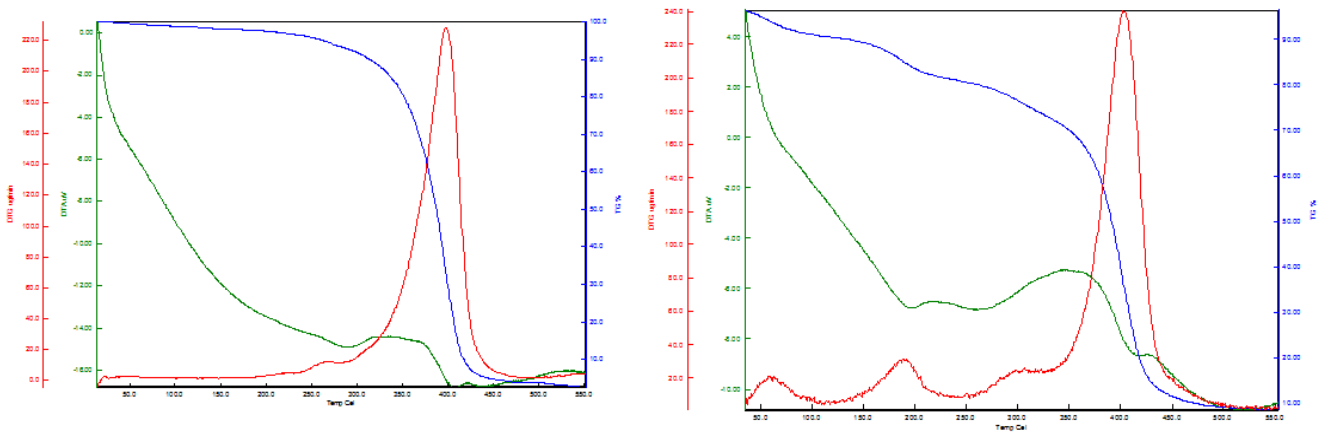

Figure 2: TGA result of toner produced with combustion (left) and combinational (right) sample.

This temperature does not seem to be appropriate for starting penetration and will require a temperature of about 1300 centimeters. Fortunately, the synthesized sample has a yellow color in the same way after the heat treatment. This means that in this specimen, before the formation of the zirconium silicate crystalline phase, the dopant is located around the host network's amorphous particles and through thermal conduction it has easily penetrated into the host network due to the numerous defects of the network. The visual color of the citrated and glycine synthesized sample is shown in Figure 3.

Studies have shown that the angularity of the toner particles increases the cleaning power of the toner residues on the light-sensitive drum after the printing process, and in turn, the toner particle surface uniformity increases the efficiency of particle transfer.

Figure 3: The visual color of the citrated (right) and glycine (left) synthesized sample.

By examining the bases of electrophotographic printing, we find that the spherical shape of the toner particles is what is expected as an end product of the in situ suspended polymerization chemical production, although it performs best in transporting the toner particles during the printing process but has problems such as weak residual toner particles on the light-sensitive receptor and, on the other hand, the angularity and non-uniformity of the surface of the toner particles produced by traditional or mechanical methods, despite being well-cleanable on the surface of the light-sensitive drum, but poor portability [15]. Therefore, it can be said that due to the importance of each of the above mentioned features, each of which can greatly affect the quality of the print, the intermediate boundary of these two properties is the particles whose appearance is semi-spherical [16].

Figure 4 shows the SEM images of the synthesized toners. The results show that the toner particles are composed of dense and spherical masses. The size of these spherical particles reaches a maximum of 10 μm. This value is less than the standard size specified and these toners can be used easily in printing. In addition, the images show that the surface of the particles is rough. This phenomenon can be attributed to the stretching of the components of this toner and their migration from the inner to the surface.

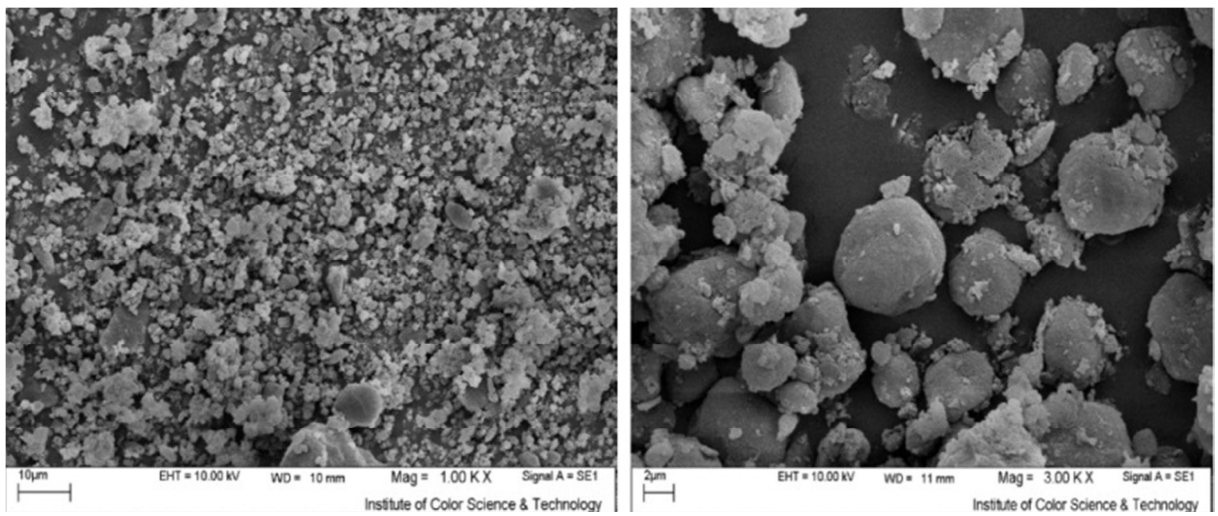

Figure 4: SEM images of synthesized toner.

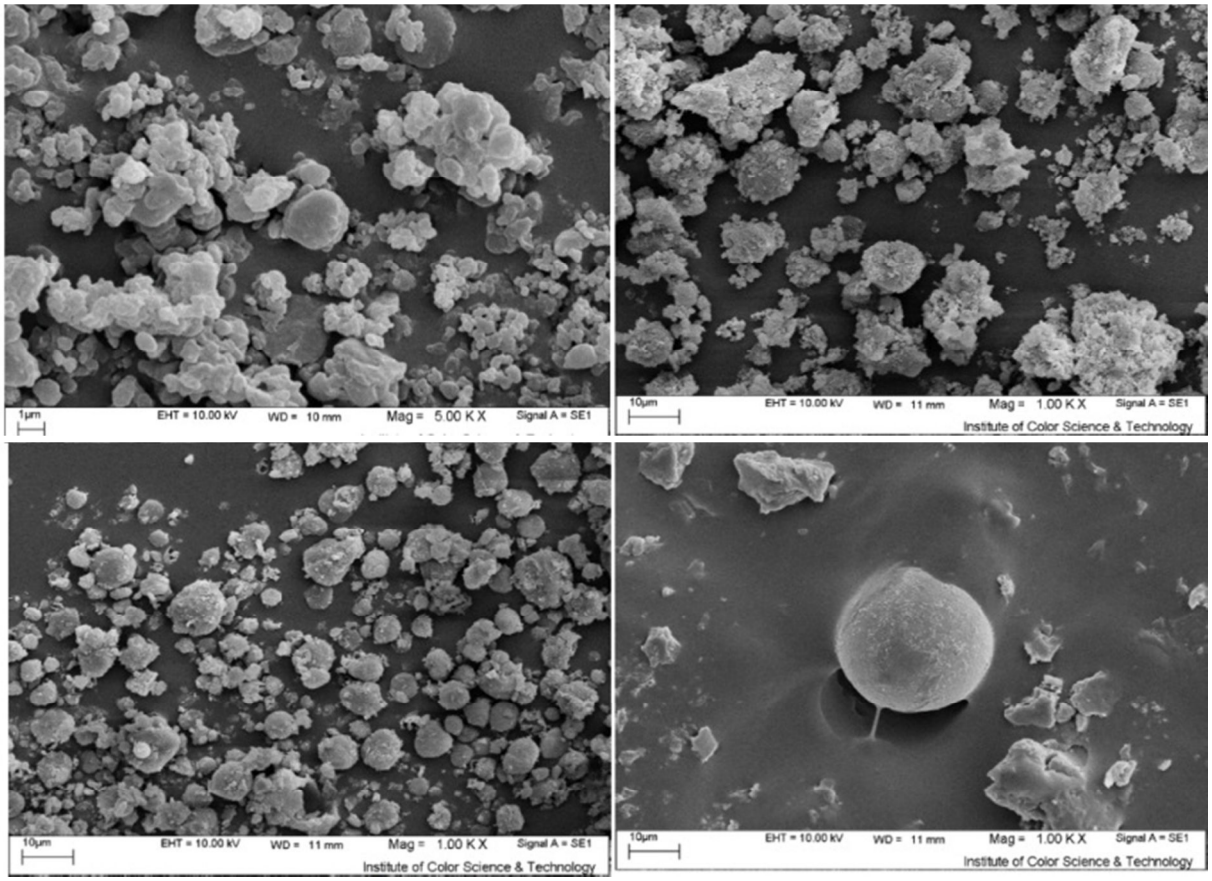

Figure 4: Continue.

4. Conclusion

ink in the printing industry are divided into two parts: public and security. One of the general composites is ceramic inks. With ceramic inks, it is possible to print directly on the tile, glass, as well as the indirect method. Today, with the help of new ceramic toners and commercially available digital printing technology, high quality, cost effective ceramic prints can be easily and quickly printed. The production of ceramic toners was done by suspension polymerization. The purpose of this study was to produce a ceramic toner. Accordingly, the use of combustion method was introduced as an efficient method for the synthesis of the predesium silicate pigment. The sample synthesized with citric acid fuel had the best color purity because of breaking the TEOS bonds. The use of nitrate sources also makes this important. Toner preparation was done by using an aggregation method called emulsion which was obtained from the morphology of spherical and dense particles.

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