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Preparation of Ceramic Toner by Suspension Polymerization

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Abstract. *In ceramic decoration by xerography, once the toner particles have been deposited, the substrates need to be subjected to thermal treatment at temperatures above* 600°C *to eliminate the organic constituents and enable the inorganic constituents to be integrated into the ceramic surface. The inorganic component includes a fraction that is able to modify the aesthetic appearance and a fraction that facilitates fusibility and integration into the substrate. At present, this type of toner is made by the pulverization method, with the presence of irregularly shaped particles and inorganic particles that are only partly coated by the polymeric matrix, which can lead to problems of particle flowability and electrical conductivity. This article describes a new method of ceramic toner preparation by suspension polymerization that avoids the above problems. The method allows a high inorganic component content in the toner composition to be reached, assuring good color saturation in decoration. © 2012 Society for Imaging Science and Technology.*

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INTRODUCTION

A toner is a dry developer widely used in copiers and laser printers. It is based on the electrophotographic process (or xerography) invented by Carlson in 1938.[1] Good quality toners should have average particle sizes around 10 μm or less, a narrow particle size distribution, a low fixing temperature with wide latitude, and sufficient surface charge.[2]

The xerographic printing technique consists of selectively depositing a powdered ink (toner) on the substrate to be decorated.[3] This is done by means of a photoconductive roller, on which the latent image is formed as electrostatic charges. The developer roller (in the case of a two-component toner) contains a mixture of toner and carrier. During the mixing of the two components, the toner develops an electric tribocharge by friction. As a result of this charge and the application of a voltage difference between the rollers, the charged toner is transferred to the photoconductive roller. An intermediate conditioning roller customarily lies between the developer roller and the photoconductive roller. The magnetic properties of the carrier cause this to remain on the developer roller. Toner transfer from the photoconductive roller to the transfer roller occurs as a result of a voltage difference. The transfer roller deposits the toner particles on the surface to be decorated. During this process, exposure to heat and pressure provisionally fixes the image to the substrate.

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 ceramic toner must, therefore, contain inorganic pigments that provide coloration and a flux (frit) that facilitates pigment integration into the glassy surface at high temperature. 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. In addition, the toner composition needs to include a polymer material with a suitable glass transition temperature that allows it to be fixed to the substrate with a small amount of energy. A resin binder is selected that will decompose well in the firing range without producing any residue that might prevent good bonding to the ceramic or glass.[4]

Different techniques are available for preparing toner particles.[5] These may be grouped into two families: the traditional method, which is based on pulverization, and polymerization methods.

Conventionally, toners for development of electrostatic charge patterns have been manufactured by fusion-mixing pigments into thermoplastic reins, to be dispersed uniformly therein, followed by pulverization and classification into desired particle sizes by means of micropulverizers and a classifier. This method is the so-called traditional (top-down) method.

The fabrication of ceramic toners by the traditional method is described by various authors.[6,7] Variants of this procedure have been reported, such as the preliminary preparation of a coloring agent obtained by sintering the inorganic pigment with a flux,[8] or even the preparation of two different types of toner by the traditional method, one containing the pigment and the other the flux.[9]

Ceramic toner preparation by the traditional method presents a series of drawbacks. The inorganic components, such as the pigments and frits, display a different fracture

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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, such as *in situ* polymerization (bottom-up); these polymerization methodologies have been well studied.[10] Patented polymerization methods for toner preparation include suspension polymerization, emulsion polymerization, dispersion polymerization, interface/free radical polymerization, and aggregation processes. All of these methods build the toner particles from droplets of monomers or micelles directly, which is distinct from breaking down from bulk materials. The polymerization process yields small, generally round, polymer particles that can be isolated from the reaction medium.[11]

These polymerization methods, which are highly developed for toners that use organic colorants, have not reached ceramic toners owing to the complexity of the presence of inorganic particles during the polymerization process.[12] Only one flocculation method and one emulsion polymerization method have been identified: Durford[13] prepared a ceramic toner by a method consisting of the flocculation of an organic polymer from an aqueous suspension of this material and inorganic pigment and frit particles. The ceramic color content reached values of 60–90% by weight. The ceramic color consisted of the inorganic pigment and frit. Kmiecik-Lawrynowicz[14] described a ceramic toner prepared by a method of emulsion polymerization from ceramic pigments with hydrophilic surface modification and polymeric resins. These toner particles reached percentages of ceramic pigment ranging from 2 to 18% by weight.

The use of a method of toner synthesis by suspension polymerization would avoid the disadvantages of the traditional synthesis method. The suspension polymerization method has the advantages of preparing toner particles with perfectly spherical shape and narrow particle size distribution.[15,16] This study describes a method of suspension polymerization for preparing ceramic toners[17] that contain an high percentage of ceramic pigment and frit in their composition and have small and narrow particle size distributions.

EXPERIMENTAL

Materials

Analytical grade styrene (St) and n-butyl acrylate (nBA), used as polymerization monomers, were purchased from Sigma-Aldrich and used without further purification. Benzoyl peroxide (BPO), used as an initiator, was also supplied by Sigma-Aldrich. The negative charge control agent (CCA), to give the toner particles appropriate electrostatic properties, was supplied by Chemos GmbH. The paraffin wax, used as a release agent with a low melting point, was from Repsol YPF Lubricantes y Especialidades, S.A. Magenta pigment ($d_{50} = 3.92$ µm) and glass frit ($d_{50} = 4.40$ µm) were supplied by Esmalglass-Itaca group and Endeka Ceramics S.A., respectively. Poly(vinyl alcohol) (PVA, Kurasay Specialties Europe GmbH) and sodium dodecyl sulfate (SDS, Sigma-Aldrich) were used as the suspension stabilizer and costabilizer, respectively.

Table I. The standard polymerization recipe.

Phase	Composition (parts)
Dispersion phase	
St monomer	107
nBA monomer	53
BPO	4.8
CCA	1.6
Wax	5
Pigment and frit	80
Continuous phase	
Water	1200
PVA	4.8
SDS	0.1

Preparation of the ceramic toner

The recipe for the synthesis of the polymerized toner is given in Table I. Styrene and n-butyl acrylate monomers were added to a 500 mL beaker. Then, paraffin wax was added and the mixture was heated to dissolve the wax. When the paraffin wax had completely dissolved the mixture was left to cool to room temperature. A CCA and BPO were then added to the monomers at room temperature. The pigment and frit were subsequently added to the mixture and dispersed in an ultrasonic bath for ten minutes. No temperature rise was observed during the ultrasonic treatment. The dispersion phase was then transferred to a 2000 mL beaker in which PVA and a surfactant had previously been dissolved in deionized water. The resulting mixture was mechanically stirred at a constant speed of 6000 rpm for 10 min at room temperature to homogenize the mixture. The homogeneous mixture was transferred to a 2000 mL polymerization reactor. The polymerization reaction was carried out in a constant temperature water bath at a setting temperature of 70–80°C for 12 h at a constant speed of 250 rpm. The final product was washed with deionized water until the supernatant was transparent. It was then vacuum filtered and dried under ambient conditions to obtain the polymerized toner.

Characterization

The particle size distribution of the samples of synthesized toner was determined with a Malvern Mastersizer 2000 laser diffraction instrument.

The particle morphology, as well as the integration of the frit and pigment particles inside the toner particles, was studied by electron microscopy. In order to favor sample conductivity, some of the samples were coated with platinum in a Balzers SCD 040 metallizer. The samples were observed and photographed with the backscattered electron and secondary electron signals of a Quanta 200F field-emission gun environmental scanning electron microscope (FEG-ESEM). Observation was performed with electrons accelerated at different voltages, namely 5, 10, and 20 kV; the lower the electron acceleration voltage was, the more superficial, therefore, the observed signal was. The samples were analyzed with an energy-dispersive X-ray microanalysis instrument with a Si(Li) detector, EDAX Genesis 7000 SUTW (super-ultrathin window), connected to the electron microscope.

Infrared spectra were collected using a Fourier transform infrared spectrophotometer (FTIR) by Thermo model Nicolet 6700. The infrared spectra were measured with a resolution of 4 cm^{-1}, and accumulated 64 scans.

The loss on ignition of the synthesized material was determined by thermogravimetry tests. The tests were performed in a Mettler model TGA/SDTA 851e simultaneous thermal analysis instrument. For this characterization, the sample was introduced into a platinum crucible and subjected to a thermal cycle in dynamic air atmosphere. The heating rate was 10°C/min and the maximum temperature was 1205°C.

The glass transition temperature (T_g) of the synthesized samples was determined by differential thermal analysis, using the above Mettler model TGA/SDTA 851e instrument. In this characterization, a dynamic nitrogen atmosphere and a thermal cycle between 25 and 200°C were used.

The ability of the synthesized samples to charge electrostatically was determined by triboelectric tests. This was done by first mixing 4% by weight of the synthesized toner sample with 96% by weight of a commercial ferrite powder carrier in a plastic container. The toner was tribologically activated by agitating the container on rollers that rotated at 85 rpm. The tribocharge acquired by the toner after 60 min on rollers was determined by the so-called blow-off method. A Faraday box was used to isolate the sample, and a Keithley model 6517B electrometer was used to determine the electrostatic charge retained in the box. A compressed air flow was used to remove the toner from the carrier and to force the toner to exit the cage. The carrier was retained in the cage by the screen. The mass lost and the resultant charge on the Faraday cage were measured, and, thus, the average q/m of the mixture was calculated. The values obtained were expressed in units of μC/g.

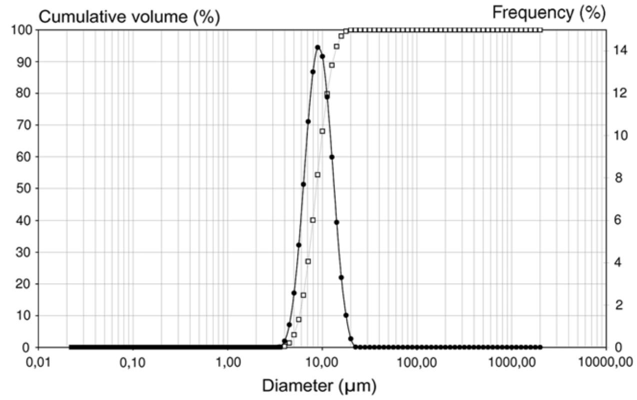

Figure 1. Particle size analysis of the synthesized toner sample: ● cumulative volume (%), ☐ frequency (%).

Table II. Characteristic diameters of the sample.

Sample	d_{90} (μm)	d_{50} (μm)	d_{10} (μm)
Synthesized toner	11.8	7.58	4.85

RESULTS

A ceramic toner was prepared by suspension polymerization according to the procedure described above. Inorganic pigments and a frit with hydrophobic behavior were used to assure high pigment and frit content inside the toner particles. The synthesized toner particles were characterized and the results are set out below.

The particle size distribution of the synthesized toner sample is shown Figure 1. The square dots represent the percentage of the total volume of particles with a diameter below D_i (cumulative volume, %). The circle-shaped dots represent the percentage by volume corresponding to particles with a diameter between D_{i+1} and D_i (frequency). Table II presents the d_{90}, d_{50}, and d_{10} parameters of the sample, these being the diameters below which there were 90%, 50%, and 10% by volume, respectively, of the total particles. It may be observed that the sample exhibited a narrow particle size distribution, in which 90% of the particles had diameters below 11.8 μm. These size and distribution characteristics suggest that this toner could yield high-quality prints.

The FTIR spectra of the obtained suspension polymerized toner (a) and of the inorganic particles of magenta pigment (b), flux (c), styrene (d), and n-butyl acrylate (e) monomers used are shown in Figure 2. The FTIR spectrum (a) displays the characteristic absorption bands of the styrene-n-butyl acrylate copolymer and the absorption bands mainly of the magenta pigment particles (897, 858, 791, and 555–461 cm^{-1}), which comprise the majority component of the inorganic fraction, and also the corresponding bands of frit (broad band around 1024 cm^{-1}). As can be seen, the C=C absorption bands of n-butyl acrylate and styrene (1630 and 1620 cm^{-1}, respectively) are not present in the FTIR spectra of the polymerized toner, where the corresponding absorption bands of styrene-n-butyl acrylate

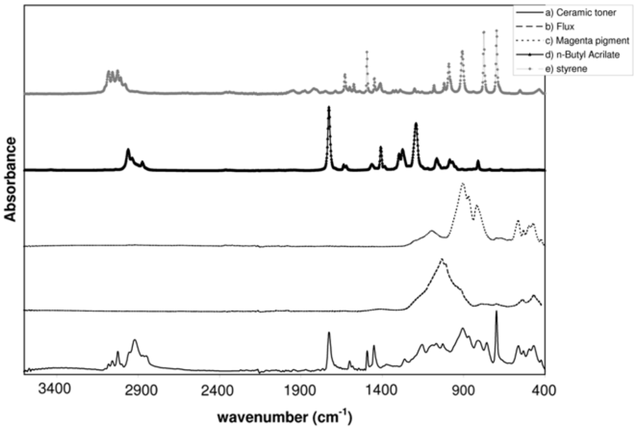

Figure 2. FTIR spectra of the toner obtained by suspension polymerization (CPT ceramic toner) (a), flux (b), magenta pigment (c), n-butyl acrylate monomer (d), and styrene monomer (e).

copolymer (1720 cm^{-1} (C=O), 1590, 1490, 1450, and 1027 cm^{-1}, corresponding to the benzene ring) are observed. Therefore, the formation of polymerized particles which contained inorganic particles was confirmed.

The obtained powder was observed in the scanning electron microscope to see the shape and size of the particles, and the integration of the inorganic particles inside the toner particles. Figure 3 shows two images of the same synthesized toner sample, taken in the scanning electron microscope with the backscattered electron signal. The backscattered electron signal provides information on the topography and composition. The signal strength increases as the average atomic number of the sample increases, so that the lightest-colored areas contain the heaviest elements (composition contrast). The light-colored areas therefore correspond to the pigment and frit signals, while the darkest colors correspond to the polymer signal. The image on the left was obtained from an electron beam accelerated at a voltage of 5 kV, whereas in the image on the right the electrons were accelerated at a voltage of 20 kV. The lower the electron acceleration voltage, the more superficial the signal is. The image on the left shows that toner particles with spherical shapes and high polymer content at the surface were obtained, which could improve the electrostatic charge of the particles. The image on the right (greater signal depth) shows that the toner particles contained high percentages of pigment and frit particles, which would yield good color strength in decoration.

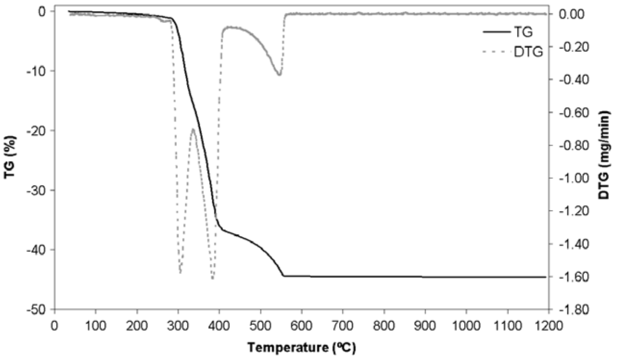

Figure 4. Thermogravimetric analysis (TG) of the synthesized toner sample and differential thermal analysis (DTG).

In order to evaluate the inorganic component (pigment and frit) content retained in the synthesized toner, a thermogravimetric analysis was performed. The obtained result is shown in Figure 4. The TG curve displays a loss on ignition of 44.6% between 20 and 1200°C, which indicates the presence in the sample of 55.4% weight of inorganic components (pigment and frit) of the total content. This high retained inorganic component content in the toner particles would allow acceptable color saturation to be achieved after the ceramic firing process.

The thermogravimetric analysis indicates, furthermore, that the analyzed sample stopped losing weight above 600°C. 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.

The differential thermal analysis performed under the foregoing conditions showed a glass transition temperature (T_g) of 47°C. The application of pressure at a temperature above the T_g value allows the polymer to soften and to

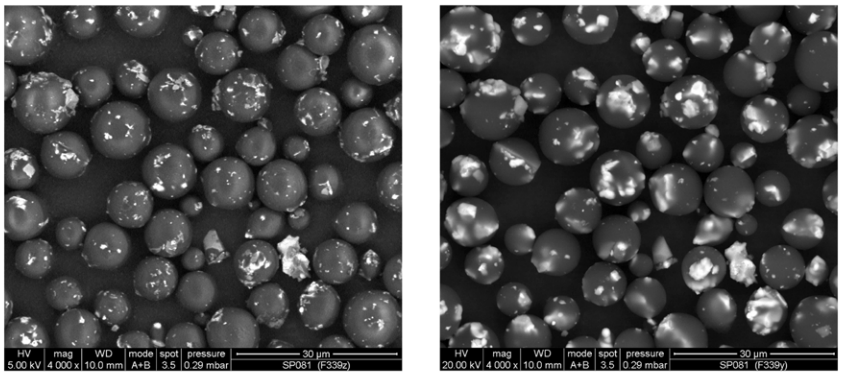

Figure 3. Images taken of the same sample in the scanning electron microscope at two different voltages: left 5 kV, right 20 kV.

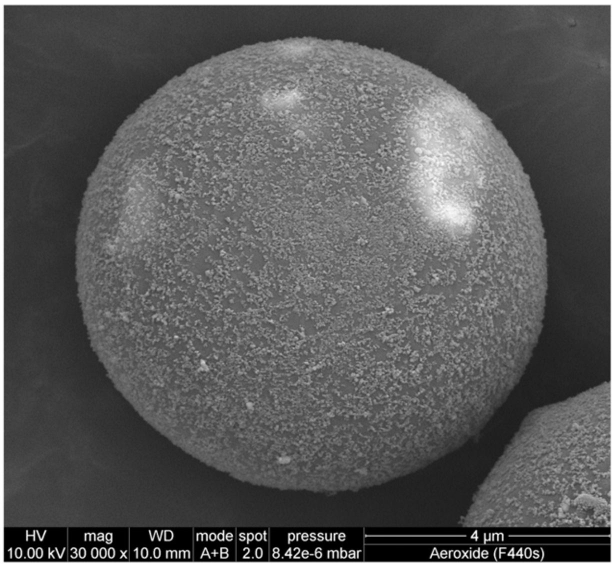

Figure 5. SEM image of a toner particle after the surface treatment.

provisionally adhere to the substrate. This adhesion enables prints in several colors to be superimposed.

In order to enhance toner powder flowability, external nanometric silica additive was used. The toner particles were mixed with 0.5% weight of silica by agitating the container on rollers for two hours. This type of additive prevents particles from approaching each other too closely for van der Waals forces to be effective, thus preventing particle agglomeration. The surface of the toner particles with external additives was observed also in the scanning electron microscope. As can be seen in Figure 5, silica nanoparticles are well distributed over the surfaces of the particles.

Four per cent by weight of the toner (with the silica addition) was mixed with 96% by weight of a commercial ferrite powder carrier. The determination of the charge/mass ratio yielded averaged values of −30 μC/g after 60 min of agitation; this charge value was maintained when the agitation time was increased (the measurement was repeated five times).

Printing tests were carried out in a xerographic printing prototype directly over a fired enameled ceramic tile. In this printing prototype the toner is transferred from the transfer roller to the surface of a tile that has been heated at 100°C. The resolution of the printed image was 600 dpi. Then the decorated tile was fired at 1100°C. Figure 6 shows a ceramic tile decorated with the magenta ceramic toner synthesized by suspension polymerization. The printed image had a good resolution, good saturation of color, and good adhesion over the fired tile.

The line acuity and optical density of the print patterns are shown in Figure 7. Fig. 7 shows the solid density from the synthesized toner. As can be seen, the toner synthesized by suspension polymerization shows thin lines after printing and firing of the tile, which means uniform triboelectric charges, uniform distribution of pigment particles in the synthesized toner, and good integration of the pigment in the enameled tile after firing.

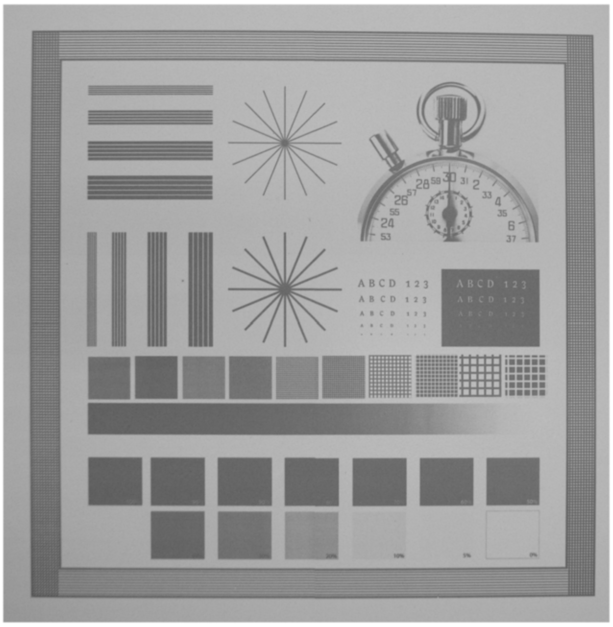

Figure 6. Image of a decorated tile using the synthesized toner.

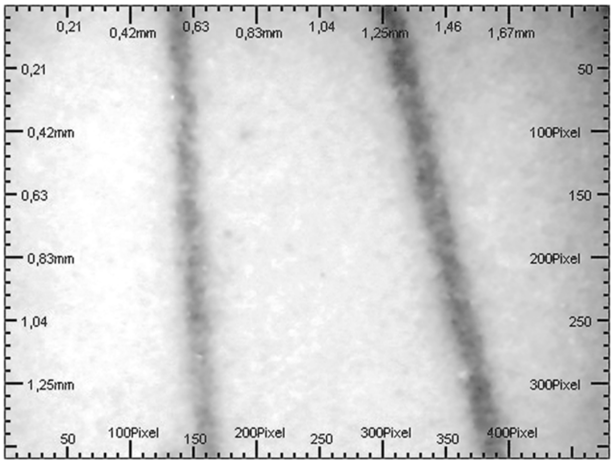

Figure 7. A photograph of lines of the printed tile shown in Fig. 6 by a digital microscope.

CONCLUSION

Ceramic toner was synthesized by suspension polymerization for the first time. The resulting toner displayed a high percentage of inorganic components; these will be the components that remain after the firing process and provide the color to the decorated piece. The synthesized toner was completely characterized. The characterization suggests that it would perform well during its application by xerography and after the firing process of the ceramic piece. The synthesized toner tested using a xerographic printing prototype.

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REFERENCES

[1] L. B. Schein, *Electrophotography and Development Physics* (Springer-Verlag, New York, 1992).

[2] D. A. Hays, "The evolution of color xerographic development systems," J. Imaging Technol. **17**, 252 (1991).

[3] Asahi Glass Co Ltd, "Color toner for electro printing, and process for producing glass plate provided with ceramic color print," employing it, US2008254268 (2008-10-16).

[4] Océ digital printing, *The Professional's Guide to Digital Printing* (Océ Pinting Sstems, Poing, 2006).

[5] C. B. Duke, J. Noolandi, and T. Thieret, "The surface science of xerography," Surf. Sci. **500**, 1005 (2002).

[6] M. Zimmer, "Method and colour compositions to produce decorated ceramic and glass products," WO9839272 (1998-09-11).

[7] Schott Glas, "A ceramic toner transferable to a high temperature resistant glass, glass or ceramic substrate by electrophotographic printing useful for the decoration of ceramic and glass products," DE10200412 (2003-07-24).

[8] Ricoh Company Ltd, "Toner composition and use thereof for forming sintered pattern on solid surface," US5976736 (1999-11-02).

[9] J. Hasegawa, N. Yanagida, and M. Tamura, "Toner Prepared by the direct polymerization method in comparison with the pulverization method," Colloids Surf. A **153**, 215 (1999).

[10] O. Masahisa, M. Masayoshi, A. Masumi, T. Masaaki, and I. Tsutomu, "Magnetic toner prepared by the suspension polymerization method," J. Imaging Sci. Technol. **38**, 415 (1994).

[11] Agfa-Gevaert N.V., "A method for electrostatographically producing master images for decoration of ceramic objects," EP0851306 (1998-07-01).

[12] Y. Duan and Q. Zhang, "Preparation of suspension polymerized color toners and correlation between ingredients and rheological behavior," J. Imaging Sci. Technol. **48**, 6 (2004).

[13] Cookson Matthey Ceramics PLC, "Toner containing inorganic ceramic color," US6110632 (2000-08-29).

[14] Xerox Corporation, "Emulsion aggregation toner compositions having ceramic pigments," EP1975728 (2008-10-01).

[15] H. G. Yuan, G. Kalfas, and W. H. Ray, "Suspension polymerization," J. Macromol. Chem. Phys. **C31**, 215 (1991).

[16] E. Vivaldo-Lima, P. E. Wood, A. E. Famielec, and A. Penlidis, "An updated review on suspensión polymerization method," Ind. Eng. Chem. Res. **36**, 939 (1997).

[17] AICE, "Integra Synergy System S.L. Procedimiento para obtener un toner cerámico y toner cerámico obtenido," P201130189, (2011-02-11).