Preparation of Chemically Prepared Toners (CPT) by Polymerisation for Ceramic Decoration

C. Ribes, Y. Bautista, V. Sanz. Instituto de Tecnología Cerámica; Castellón, Spain

Bono, J.V. Integra Synergyc System, S.L.; Villarreal, Spain

Abstract

In ceramics decoration by xerography, once the toner particles have been deposited, the substrates need to be subjected to thermal treatment at temperatures above 400 ºC to eliminate the organic constituents in the toner and enable the inorganic constituents to be integrated into the ceramic surface. The inorganic component includes an active inorganic fraction in decoration that is able to modify the aesthetic appearance of the surface to be coated, and an inorganic fraction that facilitates fusibility and integration into the substrate.

At present, this type of toner is made by the pulverisation method, with the presence of irregularly-shaped particles and inorganic particles that are only partly coated by the plastic organic matrix, which can lead to problems of particle flowability and electrical conductivity.

This paper describes a new method of ceramic toner preparation by suspension polymerisation that avoids the above problems. The method allows a high inorganic component content in the toner composition to be reached, assuring good colour saturation in decoration.

Introduction

The xerographic printing technique consists of selectively depositing a powdered ink (toner) on the substrate to be decorated [1]. 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, the exposure to heat and pressure provisionally fix the image to the substrate.

In ceramics and glass decoration, these substrates need to be subjected to a subsequent thermal treatment at temperatures above 400 ºC 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 that facilitates pigment integration into the glassy surface at high temperature. The quantity of inorganic pigments contained in the toner particles needs to be as high as possible in order to assure good colour 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. The surface of the toner particles needs to be relatively easily electrostatically chargeable.

Different techniques are available for preparing toner particles [2]. These may be grouped in two families: the traditional method, which is based on pulverisation, and polymerisation methods.

In the so-called traditional (top-down) method, all components are mixed at a temperature above the fusion temperature of the resin used. The melt is cooled, cut, and subsequently pulverised and classified to obtain small particles of the desired size.

The fabrication of ceramic toners by the traditional method is described by various authors [3], [4]. Variants of the same procedure have been reported, such as the preliminary preparation of a colouring agent obtained by sintering the inorganic pigment with a flux [5], or even the preparation of two different types of toner by the traditional method, one containing the pigment and the other the flux [6]. 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 [7].

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 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* polymerisation (bottom-up).

Generally in the polymerisation methods a dissolution, dispersion, or emulsion of the polymerisable monomer is prepared in a liquid medium, together with the other additives needed to provide the necessary properties (colorants, charge control agents, dispersants…). The polymerisation process yields small, generally round, polymer particles that can be isolated from the reaction medium.

These polymerisation 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 polymerisation process. Only one flocculation method and one emulsion polymerisation method were identified: Durford [8] 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 colour content reached values of 60–90% by weight. The ceramic colour consisted of the inorganic pigment and frit. Kmiecik-Lawrynowicz [9] described a ceramic toner prepared by a method of emulsion polymerisation from ceramic pigments with hydrophilic surface modification and from polymeric resins. These toner particles reached percentages of ceramic pigment ranging from 2 to 18% by weight.

The emulsion polymerisation process is known to present certain disadvantages, such as the difficulty of eliminating the surfactants and emulsifiers used; and the difficulty of controlling the particle size distribution, obtaining wide distributions, therefore making it difficult to control the quality of the obtained products by the polymerisation process.

The use of a method of toner synthesis by suspension polymerisation would avoid the disadvantages of the traditional synthesis method, as well as those presented by emulsion polymerisation. This study describes a method of suspension polymerisation for preparing ceramic toners [10] that contain a high percentage of ceramic pigment and frit in their composition and have narrow particle size distributions.

Experimental

Preparation of the ceramic toner

The recipe for the synthesis of the polymerised toner is given in Table 1. Styrene and n-butyl acrylate monomers were added to a 500mL 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 (charge control agent) and BPO (benzoyl peroxide) were then added to the monomers at room temperature. The pigment and frit were subsequently added to the mixture and dispersed in the presence of ultrasonic energy. The continuous phase was then transferred to a 2000mL beaker in which PVA and a surfactant had previously been dissolved in deionised water. The resulting mixture was mechanically stirred at a constant speed of 6000rpm for 10 min to homogenise the mixture. The homogeneous mixture was transferred to a 2000mL polymerisation reactor. The polymerisation reaction was carried out in a constant temperature water bath at a setting temperature of 70-80 ºC for 12h. The final product was washed with deionised water until the supernatant was transparent. It was then vacuum filtered and dried to obtain the polymerised toner.

Table 1. Standard Polymerisation Recipe

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

Characterisation

The particle size distribution of the samples of synthesised toner was determined with a MALVERN MASTERSIZER 2000 laser diffraction instrument.

Particle morphology, as well as the integration of the frit and pigment particles inside toner particles, was controlled by electron microscopy. In order to favour sample conductivity, some of the samples were coated with platinum in a Balzers SCD 040 metalliser. The samples were observed and photographed with the backscattered electron and secondary electron signal 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, the more superficial was, therefore, the observed signal. The samples were analysed with an energy-dispersive X-ray microanalysis instrument with a Si(Li) detector, EDAX Genesis 7000 SUTW (super ultra thin window), connected to the electron microscope.

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

The glass transition temperature (Tg) of the synthesised samples was determined by simultaneous thermal analysis, using the above Mettler model TGA/SDTA 851e instrument. In this characterisation, a dynamic nitrogen atmosphere and a thermal cycle between 25 ºC and 200 ºC were used.

The ability of the synthesised samples to charge electrostatically was determined by triboelectric tests. This was done by first mixing 4% by weight of the synthesised 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 minutes 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. The values obtained were expressed as the charge/mass (q/m) ratio in units of μC/g.

Results

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

The particle size distribution of the synthesised 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 diamond-shaped dots represent the percentage by volume corresponding to particles with a diameter between D_{i+1} and D_i (frequency). Table 2 presents the d_{90}, d_{50}, and d_{10} parameters of the sample, these being the diameters below which there was 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.

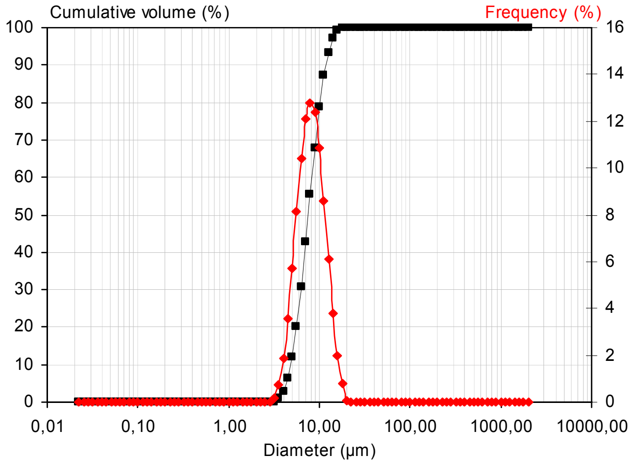

***Figure 1**. Particle size analysis of the synthesised toner sample*

Table 2. Characteristic diameters of the sample

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

Figure 2 shows two images of the same synthesised toner sample, taken in the scanning electron microscope with the backscattered electron signal. The backscattered electron signal provides information on the topography and composition. Signal strength increases as the average atomic number of the sample increases, so that the lightest-coloured areas contain the heaviest elements (composition contrast). The light-coloured areas therefore correspond to the pigment and the frit signals, while the darkest colours 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 is the signal. The image on the left shows that toner particles with spherical shapes and a high polymer content at the surface were obtained, which could improve 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 colour strength in decoration.

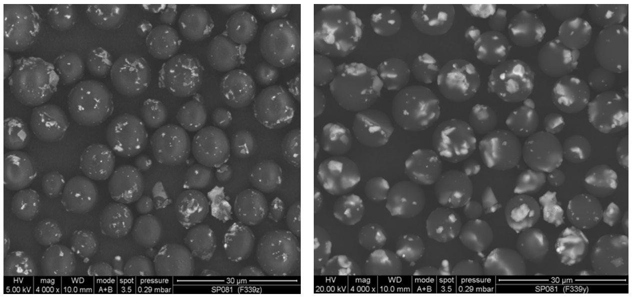

***Figure 2**. Images taken of the same sample in the scanning electron microscope at two different voltages: left 5 kV, right 20 kV*

In order to evaluate the inorganic component (pigment and frit) content retained in the synthesised toner, a thermogravimetric analysis was performed. The obtained result is shown in Figure 3. The TG curve displays a loss on ignition of 44.6% between 20 ºC and 1200 ºC, which indicates the presence in the sample of 55.4% of inorganic components. This high retained inorganic component content in the toner particles could allow acceptable colour saturation to be achieved after the ceramic firing process.

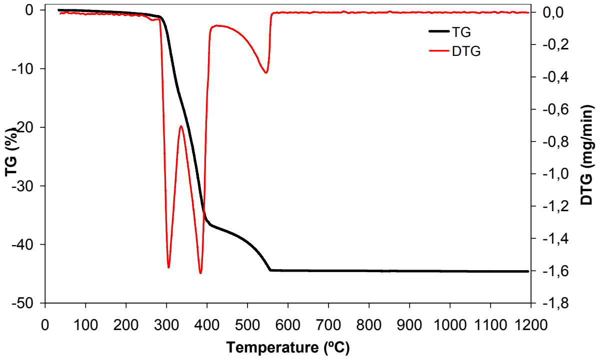

***Figure 3**. Thermogravimetric analysis of the synthesised toner sample*

The thermogravimetric analysis indicates, furthermore, that the analysed sample stopped losing weight above 600 ºC. The main polymer decomposition appeared to occur in three phases: the first at about 300 ºC; the second before 400 ºC, both with important mass losses; and the third in a wider range of temperatures, between 400 ºC and 600 ºC. The firing cycles of the samples decorated with this toner would, therefore, need to reach temperatures above 600 ºC.

The simultaneous thermal analysis performed under the foregoing conditions showed a glass transition temperature (Tg) of 47 ºC. The application of pressure at a temperature above the Tg value allows the polymer to soften and provisionally to adhere to the substrate. This adhesion enables prints in several colours to be superimposed.

In order to enhance toner powder flowability, external nanometric silica additive was used. This type of additive keeps particles from approaching each other too closely for van der Waals forces to be effective, thus preventing particle agglomeration.

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 (the measurement was repeated 5 times).

The synthesised toner properties will need to be adjusted after printing trials in a xerographic machine adapted for ceramic decoration.

Conclusion

Ceramic toner was synthesised for the first time by suspension polymerisation. The resulting toner displayed a high percentage of inorganic components, these will be the components that remain after the firing process and provide the colour to the decorated piece. The synthesised toner was completely characterised. The characterisation suggests that it could perform well during its application by xerography and after the firing process of the ceramic piece.

References

[1] Océ digital printing: The professional's guide to digital printing (Océ printing systems, 2006).

[2] C. B. Duke, J. Noolandi, T. Thieret, “The surface science of xerography”, Surface Science 500, 1005, (2002).

[3] M. Zimmer, “Method and colour compositions to produce decorated ceramic and glass products”, DE19709011, 1999-03-03.

[4] 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.

[5] Ricoh Company, Ltd “Toner composition and use thereof for forming sintered pattern on solid surface”, US 5.976.736, 1999-11-02.

[6] Agfa-Gevaert N.V “A method for electrostatographically producing master images for decoration of ceramic objects”, EP0851306, 1998-07-01.

[7] 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.

[8] Cookson Matthey Ceramics PLC, “Toner containing inorganic ceramic color”, US 6.110.632, 1997-07-07.

[9] Xerox Corporation, “Emulsion aggregation toner compositions having ceramic pigments”, EP1975728, 2008-10-01.

[10] AICE, Integra Synergy System S.L. “Procedimiento para obtener un toner cerámico y toner cerámico obtenido”, P201130189, 2011-02-11.

Author Biography

Celia Ribes received her degree in chemistry from University Jaume I (Castellón, Spain) in 2003 and her PhD in organic synthesis from the same university in 2008. Since then she has worked in the Nanotechnology Area at the Instituto de Tecnología Cerámica (ITC) in Castellón, Spain. Her work has focused on ceramic toner synthesis by polymerisation methods. She has also worked on formulating inorganic–organic hybrid materials.