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Chemical Toners from a Latex Aggregation Process

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Abstract

"Chemical" or "polymerisation" toner technologies offer the ability to manufacture small particle size (e.g. 5µm) toners by economically viable processes. ZENECA has developed a process in which polymer latices, pigments and, if desired, waxes and charge control agents, can be aggregated in a controlled manner to produce toners with a mean size from below 5 to above 10 µm. Narrow particle size distributions are attained across the size range without classification. The process allows the particle shape to be controlled from highly irregular through to spherical. The process has been used to make black and coloured toners.

Introduction

For improved resolution in colour printing and for certain monochrome printing applications, toners with diameters below those currently used have been sought. The efficiency of the conventional milling process falls, and the costs rise[1], as the particle size is reduced much below the existing range. "Chemical" or "polymerisation" toner technologies seek to access these lower particle size toners (especially 7 µm and below) by cost-effective routes.

Many processes have been advocated as routes to chemical toners, the most common being: suspension polymerisation[1,2], solution-dispersion, dispersion polymerisation[3] and latex aggregation[3]. The first three tend to produce spherical particles. This can be advantageous in some circumstances, but can give problems in toner cleaning where cleaning blades are used[3]. Dispersion polymerisation, in which the polymer precipitates from the medium, can give very narrow particle size distributions, but it is more difficult to incorporate additives (e.g. pigments, waxes and charge control agents) than with the other processes.

Latex aggregation routes offer the ability to control particle shape from irregular to spherical. In these processes aqueous resin dispersions (usually made by emulsion polymerisation) are combined with aqueous pigment dispersions and the system caused to flocculate. From the flocculated mixture are grown, by heating and stirring, aggregates of the required size. The final step is to cause coalescence of the latex particles by heating the system above the Tg of the resin.

An evaluation of suspension polymerisation, solution-dispersion and latex aggregation as routes to chemical toners was carried out. A novel latex aggregation process was developed, and this was found to give narrower particle size distributions than were obtained from either the suspension or the solution-dispersion routes. In addition the route showed the advantage of producing a good pigment dispersion throughout the toner, along with the ability to control particle shape.

Experimental

Toners were prepared by ZENECA's proprietary latex aggregation route. Particle size determinations were made using a Coulter Multsizer II. Volume Geometric Size Distributions (GSDs) were obtained from the Coulter data, and are defined as d(84.1)/d(50), where d(x) represents the diameter below which x% of the volume is contained. Similarly Dv50 and Dn50 represent the diameters (µm) below which 50% of the volume and number of particles respectively are contained.

Tribocharge measurements were made using a Toshiba TB200 blow-off machine. A silicone-coated ferrite carrier was used with the toner concentration at 6%.

Toner melt rheology was characterised using a Rheometrics RDSII melt rheometer, with a 25mm parallel plate and a 2mm plate separation. The heating rate was 10°C/min, the frequency 10 radians/second, and the strain 10%.

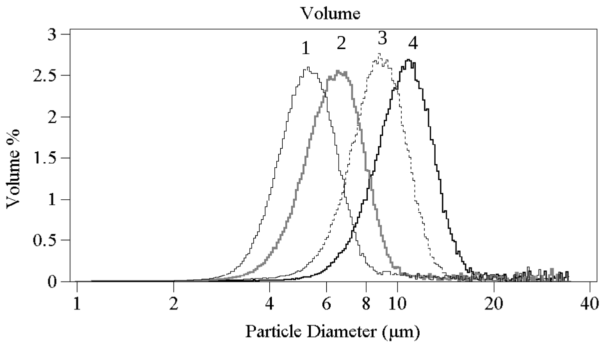

Figure 1. Volume particle size distributions for four chemical toners

Results and Discussion

Particle Size Control

By controlling the process variables in the aggregation process (e.g. the solids concentration, the temperature and the stirring rate) excellent control over the particle size was attained, from below 5 μm to above 10 μm. The particle size distributions for a series of toners are shown in Figs. 1 (volume distribution) and 2 (number distribution). No classification process was used. The numerical data are given in Table 1. The graphs show that using this process narrow particle size distributions can be attained across the size range, with the GSDs lying in the range 1.22-1.24. This ability to control particle size whilst maintaining narrow distributions has been demonstrated for cyan, magenta, yellow and black toners.

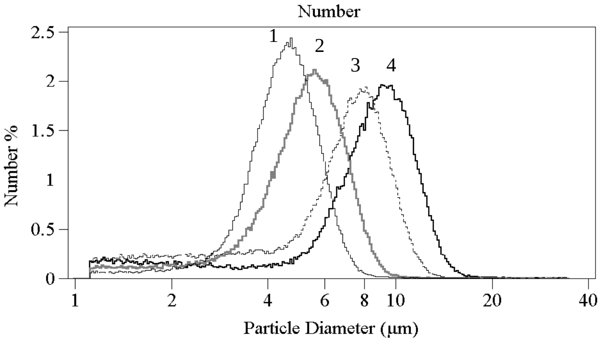

Figure 2. Number particle size distributions for four chemical toners

Table 1. Particle Size Distribution Data for Four Chemical Toners

Toner	Dv50 (μm)	Dn50 (μm)	Dv50/ Dn50	GSD (vol)
1	5.3	4.5	1.17	1.24
2	6.4	5.3	1.21	1.23
3	8.7	7.0	1.25	1.22
4	10.6	8.6	1.23	1.22

Particle Shape Control

By controlling the process conditions it is possible to vary the particle shape from highly irregular through to spherical. Two examples are shown in Figs. 3 and 4. The particles in Fig. 3 show a smooth, but off-spherical shape, whilst those in Fig. 4 are spherical. Both toners were made from the same latex and pigment dispersion, the only difference being in the process conditions.

Colour

Important colour properties for colour toners include optical density, brightness and transparency. To achieve high transparency it is important that the pigment particle size is kept to a minimum (ideally <300nm) and that the pigment is well dispersed throughout the toner. The same factors apply to other additives such as waxes and charge control agents (CCAs). High transparency also requires that the toner is well fused, so that light is not scattered from the toner particles[4,5]. A low toner melt viscosity at the fusion temperature is clearly advantageous in this respect[5].

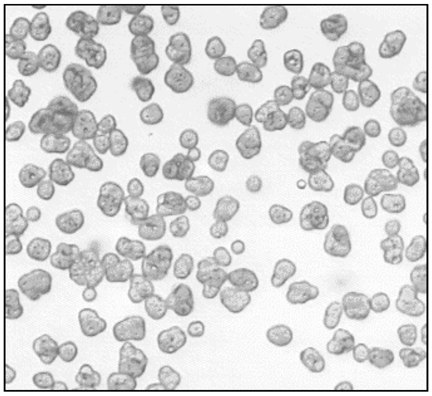

Figure 3. Optical micrograph of toner showing smooth off-spherical particles

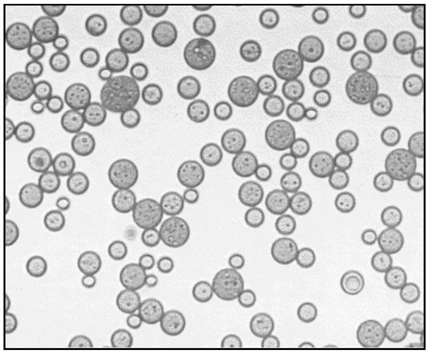

Figure 4. Optical micrograph of toner showing spherical particles

In the selection of pigments for coloured toners, several factors need to be balanced. These include: transparency, lightfastness, thermal stability and the effect on the triboelectric properties of the toner, as well as cost. For use in an aggregation process for a chemical toner it must be possible to mill the pigments in an aqueous medium to low particle size, and to obtain a stable dispersion. For cyan toners it is normal in conventional colour toners to use Pigment Blue 15:3 (β copper phthalocyanine). This pigment shows good transparency and lightfastness. For magenta toners common choices include Pigment Red 122 (dimethylquinacridone) and Pigment Red 81 (a complex metal xanthene salt). The former has the advantage of much higher lightfastness, whilst the latter tends to show higher chroma. Disazo yellows, such as Pigment Yellow 17 are a popular choice, although isoindolines (e.g. Pigment Yellow 185) have also been used.

Several coloured pigments and carbon black have been milled in water with suitable dispersants, and stable, low particle size dispersions achieved. Analysis with a Coulter LS230 particle sizer showed that in each case the majority of particles were below 200 nm.

Tribocharge

The tribocharge properties of a toner are determined by a number of factors, including: the resin type and presence of functional groups; the pigment and its distribution through the toner; the presence and nature of a charge control agent; and, if two component development, the carrier choice and the toner concentration. Charge control agents can be incorporated in the chemical toner in two ways. In the first method the CCA is flocculated along with the latex and pigment. Data for two CCAs, incorporated in the aggregation process in this way are shown in Fig. 5.

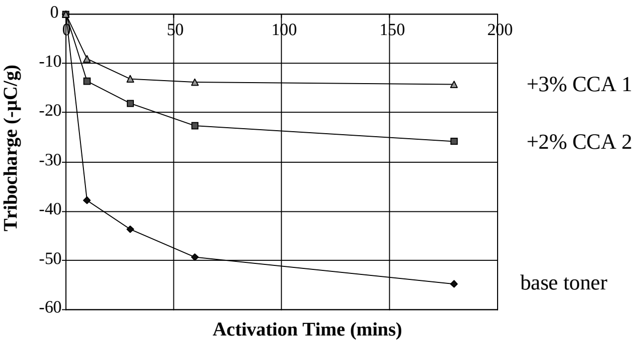

Figure 5. The effects of internal CCAs on the tribocharge response for a chemical toner

The "internal" CCA affects both the magnitude of the tribocharge and the rate of activation. In both cases a flatter activation response curve is obtained. Both Scanning Electron Microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS) indicated that the majority of the CCA was inside the particle, and very little on the surface.

The second method of CCA incorporation is to add it as an external additive, blending it with the dry toner using a high impact energy blender. Several CCAs were blended with a chemical toner made by the aggregation process. The results are shown in Fig. 6.

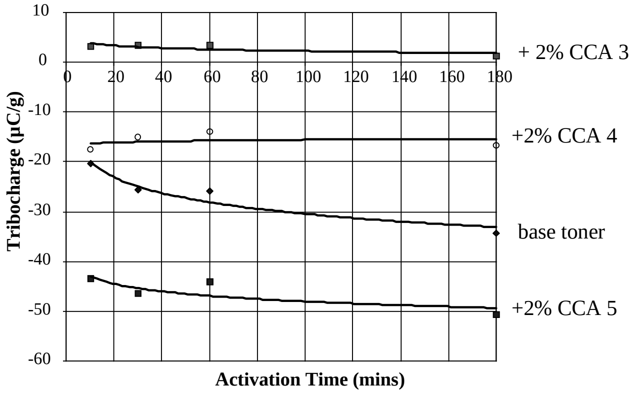

Figure 6. The effects of external CCAs on the tribocharge response for a chemical toner

By use of different CCAs the level of charging can be varied over a wide range.

Melt Rheology

The melt rheology of the toner is critical in determining its fusion characteristics, e.g. the minimum fixation and the hot offset temperatures[6]. For black toners used in monochrome printing a wide fusion latitude is desirable, and this is often achieved by using resins with broad molecular weight distributions. The resin contains a mixture of low, medium and high molecular weights, and often a proportion of cross-linked polymer. For colour it is essential for transparency that the toner particles are well fused, and so lower molecular weight resins (often polyesters) are frequently used.

Several latices have been prepared by emulsion polymerisation for use in the aggregation process. These latices have different average molecular weights, and some contain cross-linked material. By combining these latices in different proportions prior to aggregation, different overall molecular weight distributions can be attained, and so the melt rheology controlled.

Three latices were made with different average molecular weights and aggregated, along with cyan pigment, in varying proportions. The results for four toners are shown in Fig. 7. The curves cover a wide range in melt viscosity. As expected the toners richer in the higher molecular weight latices show the higher melt viscosity.

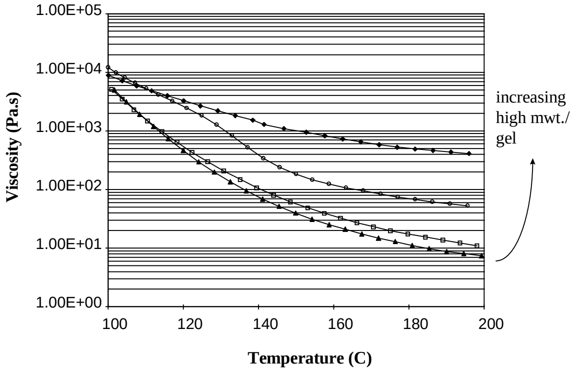

Figure 7. Melt viscosity versus temperature plots for toners with different molecular weight distributions

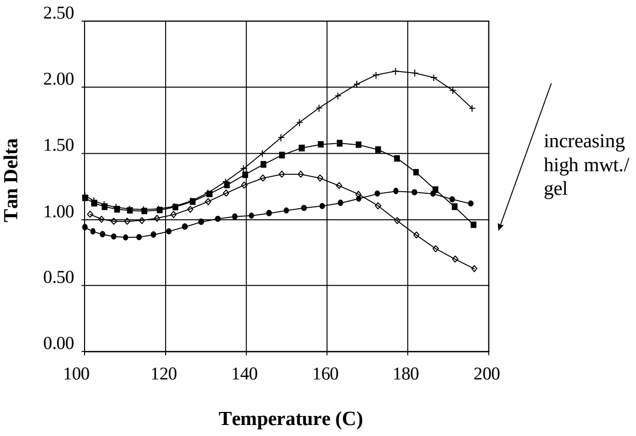

Figure 8. Tan δ versus temperature plots for toners with different molecular weight distributions

Another important rheological parameter is tan δ, and its variation with temperature[6]. For wide window toners it is desirable for the value of tan δ to be close to one across as wide a temperature range as possible. The results for four toners (different from those in Fig. 7) with different molecular weight distributions are shown in Fig 8.

By including resins with low and medium molecular weight, and either high molecular weight or gel, it is possible to achieve a toner melt rheolgy with a tan δ value close to one across the temperature range of interest.

Acknowledgements

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Biography

Martin Edwards received his BA and PhD from the University of Cambridge in 1982 and 1985 respectively. Dr Edwards joined ICI in 1985 and continued with ZENECA when the company was demerged from ICI in 1993. He has worked on a variety of polymer and coatings projects before joining the Electrophotography group in 1996.