Concerning the formation of chemical toners using a latex aggregation process.

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Abstract

A number of companies are currently producing chemical toners using latex aggregation approaches. This communication attempts to provide an understanding, based on the principles of colloid science, for each of these different processes. While the starting latex for each aggregation scheme have many properties in common, the toner that forms may show dramatic differences in the image development and fusing performance. These differences arise from the coagulant used to assemble the latex and the aggregation processes itself. The potential for future advances in this toner technology is given.

Introduction

In recent years the application of chemically produced toners (CPT) in electrophotographic (EP) technology has expanded rapidly as OEM hardware vendors implement this new toner technology. The major reason for the widespread adoption of this technology is that all CPT approaches to toner making allow for the efficient fabrication of small sized toners (less than 7 micron in diameter) with narrow size distribution. A small size toner lowers the cost per print as far less toner can be developed on a page to achieve the same image density. In contrast to conventionally jetted toners, all CPT processes give toners with no flat segments or sharp corners. This feature of a CPT particle surfaces is known to decrease undesired toner development on the photoreceptor (reduces “splatter”) and allows a higher toner transfer efficiency (TE) for the transfer of an image from the photoreceptor to the final image medium either when an intermediate transfer belt is used, or when the transfer is direct from the photoreceptor. These image transfer features provide for improved image quality over those available from conventionally produced toners.

The chemical processes that are used to manufacture CPT particles start either from small molecules (monomers), that are polymerized along with pigment and release agent to make the toner, or from pre-formed polymers. When starting from monomers, suspension polymerization may be employed to form toner sized particles directly from the starting monomers as practiced by Canon and the Zeon Corporation. This radical polymerization process is restricted to materials such as styrene and acrylates that satisfy these reaction conditions. Dispersion polymerization of monomer in an organic fluid also produces particles of the right size but that approach is not currently used to make toner particles on a commercial scale.

Two different chemical processes for forming toner start with pre-formed polymer. The first involves dissolving the chosen polymer in an organic solvent that is immiscible in water. This polymer solution is then dispersed along with a particulate colorant and a release agent (wax) into water using a surface active agent. Under appropriate conditions particles of appropriate size are formed and when the solvent is removed toner particles remain dispersed in the aqueous medium and can be separated from the water and dried. This type of process is used by Fuji Xerox in their SPSS process, Ricoh in the PxP process and by Sanyo on a commercial scale. A second process using a pre-formed polymer utilizes the material in the form of a resin dispersed in water (latex) which is assembled, along with dispersed colored pigment and wax particles, into toner sized particles using an aggregation scheme. This aggregation CPT process is the focus of the present paper which is attempt to compare and contrast the many ways of assembling a collection of small particles of the order of 200 nm in size into an object of between 5 and 7 microns in diameter. The influence of the different aggregation processes on the EP performance (particularly in development and fusing) of the resulting toner particles will be discussed.

Latex aggregation procedures

All toners made using the aggregation processes start from a polymer dispersed in water (latex). This latex forms at least 80% by weight of the final toner and its properties dominate the fusing performance of the final toner. Currently, all the latex used in forming aggregated toners is fabricated using styrene and acrylic monomers by emulsion polymerization in water using surfactants as particle stabilizers. Polymer particle dispersions made by other processes may also function as a suitable starting material but to date none have appeared in commercial toner made using an aggregation process. The latex product produced by emulsion polymerization is generally negatively charged and can have a diameter in the range from 100 to 500 nm. The composition of the polymer resin is selected using the molecular property design rules that have long been used in the design of resins for conventional toners. The most important molecular properties of the resin are the glass transition temperature, T(g), and the molecular weight, Mw. A lower T(g) resin gives a better image fix (adhesion to the final substrate) but the T(g) has to be sufficient to ensure that the final toner resists blocking in the development system and on shipping the toner from the factory to the final customer. A resin having a T(g) below 50°C will seldom satisfy the blocking requirement. The Mw of the resin controls the gloss of the final image. Higher molecular weight leads to lower final gloss. For styrene rich polymers the Mw cannot be too low as such resins are brittle and crack easily. Despite the application of these general rules the final image fusing characteristics might not be optimal as the coagulant can interact with the resin and significantly modify its fusing behavior.

CPT processes unlike conventional toner preparation using a melt mixing stage have the advantage that it is relatively easy to incorporate a release agent (wax) into the toner and not have to use excessive quantities of material into the formulation to ensure that the final size of the wax domain has the desired size for providing optimal release from the fuser. The size of the wax dispersion in the starting formulation may change during the latex aggregation process but can be compensated for if the process is understood. The location of the wax in the final particle may also be controlled and it can be located near the surface of the final particle or in the particle core as desired.

All latex aggregation procedures involve heating the aggregates above the T(g) of the resin in a coalescence phase. This process step is needed to ensure that an aggregate forms a compact particle with surface features that have lost most of their individual latex characteristics. In the coatings industry the term coalescence is used in a similar manner for the film drying stage when a layer of latex particles collapses into a continuous film. Many toner aggregates are not readily formed into spheres during coalescence even when heated to more than 90°C (well above the latex T(g) described above) as both the presence of ionic functionality and surfactants on the latex surface hinder this surface energy driven process. Heating at temperatures above the latex T(g) may also lead to considerable aggregate growth for the same reasons that a toner "blocks" above that temperature. If this particle growth is undesired it may be minimized and controlled by stabilizing the particles before heating. This may be accomplished by adding colloidal stabilizers (surfactants or fine particulates) or, for latex with weak acid or basic surface groups, by changing the pH of the coalescence environment.

The aggregation of dispersed polymer particles (latex) has been widely studied from a colloid science perspective. A particle formed by emulsion polymerization in water is stable if it carries sufficient electrical charge to be able to repel other particles in the dispersion. Most studies of colloidal stability of these systems are made by adding a salt (e.g. NaCl) to the aqueous medium and determining the critical coagulation concentration of the added salt at which significant flocculation is observed. The mechanism involved is electrostatic "screening" of the latex charge by the conductivity of the solution. At a critical salt level the extent of the electrostatic field that surrounds the particle is diminished and an attractive force (the van der Waals force) to come into play. The aggregation process for this situation is well understood at a low concentration of latex particles and is described in terms of the DLVO theory. No commercial CPT aggregation process appears to utilize simple electrostatic screening as a means to assemble the charged latex. Aggregates formed using the charge screening approach are not easily stabilized in coalescence while maintaining the aggregate integrity and very large particles tend to form on heating above the resin T(g). All commercial CPT processes utilize aggregation schemes that either employ a coagulant to modify the surface charge on the particles, or by forcing electrostatic coagulation by the addition of particles carrying a charge opposite to that found on the latex.

The surface charge of a polymer particle is usually defined in terms of the mobility of the latex in a defined field and then this value is reported as an effective surface potential, the zeta potential. The surface charge depends on the ionization state of groups on the surface which may depend on the pH of the medium if these groups behave as weak acids or bases. Latex dispersions resist aggregation if the magnitude of the zeta potential is greater than 40 mV. We will only consider anionic latex dispersions in this discussion as all the materials used in current CPT aggregation technology utilize a latex that has a negative charge. The zeta potential of the latex may be reduced if a cationic species (ion, small molecule or even a particle that is much smaller than the latex) is irreversibly adsorbed onto the particle surface. A number of cationic species show this behavior, when added in excess of the minimum required to neutralize the anionic latex charge some coagulants continue to adsorb onto the uncovered portions of the latex surface resulting in a particle with a net positive charge. If this charge is too high (>40 mV) the latex is found to be stable. The aggregation rate depends on zeta potential and usually is maximum when the surface has exactly zero charge. Aggregation is under better control if conducted at a zeta potential of between -5 and -10mV or between +5 and +10 mV rather than at the point of zero charge. The charge reversal feature is an essential characteristic for forming "core-shell" aggregates in the aggregation processes described below.

The principles of latex aggregation do not depend on the exact composition of the starting latex and rely mostly on the surface characteristic of the dispersed resin.

The first patents for latex aggregated CPT toner were assigned to Nippon Carbide by the US Patent Office and issued on January 10, 1989 [1] and February 26, 1991 [2]. The initial patent covers aggregates formed by mixing positive and negative charging resin dispersions, while the second treats the case of aggregating a resin and colorant of the same polarity. A black SCD toner made by Nippon Carbide was used in the Xerox DocuPrint 4508 laser printer. Fuji Xerox acquired the Imaging Division of Nippon Carbide in 2000 and Nippon Carbide's intellectual property.

Xerox and Fuji Xerox aggregated CPT.

Xerox initially used a cationic surfactant to aggregate anionic latex and a dispersed pigment. The latex was formed by emulsion polymerization of styrene, butyl acrylate and a small quantity of a carboxylic acid monomer without buffering giving a resin dispersed in water at a low pH (~3.5). The first of many patents on the use of a cationic surfactant as a coagulant was issued in 1994 [3]. After completing the aggregation at a temperature below T(g) and before performing latex coalescence at T >> T(g), a solution of anionic surfactant was added to the aggregated particles to stabilize against growth at the high temperature. Heating well above T(g) produces the compact and robust toner particles. In a study of model materials for this aggregation/coalescence procedure a series of papers was published by Lazar & Hesp [4a,b,c] which provides details of how the zeta potential can be changed from negative to positive with added surfactant and illustrates the dramatic growth of any aggregates that are not stabilized before performing the coalescence. Fuji Xerox [5] made a small modification to the original surfactant aggregation sequence by first coagulating the anionic latex, colorant and wax using a little more cationic surfactant than was needed to produce particles with desired size characteristics. This produces a "core" particle with a net positive charge that contains more pigment and wax than is desired in the final toner. Anionic latex is then added to this particle dispersion and is attached to the outer surface of the core particles. A thin "shell" of polymer without any pigment or wax is thus located on the aggregated particle surface. This core-shell concept results in toners that have similar charging behavior for all colors.

Fuji Xerox experimented with a number of alternate coagulants for latex aggregation as the cationic surfactant route did not at ensuring that the release agent (a poly-ethylene wax) did not migrate to the surface of the aggregate during the high temperature coalescence process. An inorganic coagulant widely used in water treatment applications was chosen to aggregate latex, pigment and wax for the next series of toners. This inorganic coagulant aluminum chlorohydrate (also known as poly-aluminum chloride) is known to be very effective at low doses. In a low pH environment this inorganic polymer consists of highly charged cationic particles with dimensions of between 2 and 10 nm [6]. The core-shell particle formation approach was followed but the process was modified by using a pH adjustment from 3.5 to 7 to replace surfactant stabilization in the coalescence stage [7]. This process modification became the approach used to form the EA (Emulsion Aggregation) Toner employed in the first Fuji Xerox full color device (DocuCentre Color 500/500 CP) launched in the Fuji Xerox marketplace in September 2001. The EA toner shows remarkable TMA (toner mass per unit area) uniformity for all the colors in a C,M,Y & K application. The gloss of this PAC aggregated toner is not as high as one made using a cationic surfactant as a coagulant but shows a far wider range between cold offset and hot offset than does the surfactant aggregated toner. It should be noted that the viscosity of carboxylic polymers partially neutralized into the form of the metal salt by ions such as magnesium and aluminum may differ dramatically from the non substituted resin [8].

EA toner has been deployed in a wide range of EP products by both Fuji Xerox and Xerox. The objective is to use CPT materials in all newly designed print engines across the whole product range. Recently, a "second generation" of this toner has been announced by Fuji Xerox. This toner is named EA HG (high grade) and it offers extended performance in those markets that require a toner giving a higher gloss image than was found with the original EA product. The EA HG toner employs a slightly modified resin (latex), a new release agent better suited to the new fusing subsystem, and is formulated using small colloidal silica in the pre-aggregate dispersion [9]. The small sized colloidal silica improves the flow of the softened toner giving the image a higher gloss without detracting from the other performance attributes of the EA toner. Other Xerox patents indicate that there are other means of achieving the behavior of the EA HG toner. The latest Xerox announcement concerning EA toner was made on April 4, 2007 when a series of monochrome print engines "Nuvera™ 100/120/144 EA Digital Production System" was disclosed. These units use an EA toner that provides a matte finish when fused and is of approximately the same size as the earlier EA toners. The 144 unit is the fastest EP print engine using a CPT toner on the market today. The technology used in this low gloss aggregated toner which incorporates a wax as a release agent is not certain but some issued patents and a number of recently published US patent applications indicate that this type of toner can be formed using slight modifications to the existing EA toner process. One means of changing a glossy toner formulation to one giving a matte finish is the use of a small quantity of cross-linked latex in the resin blend. This is particularly effective if it can be added in the formation of the "shell" on the outer surface of the toner aggregate. If this is done the blocking resistance of the toner can be improved without impacting image fix.

Konica-Minolta aggregated CPT.

Minolta, Konica and the more recent merged company, Konica-Minolta (K-M), also adopted an aggregation approach to CPT. SEM images of the toners made by K-M show many similarities to the toners made by Xerox and Fuji Xerox but examination of the patents issued to Konica, Minolta and K-M indicate the differences in the procedures used to form a Simitri™ toner. While the starting latex does not drastically differ from that used in EA Toner, in terms of the major monomers employed, it appears to utilize more carboxylic co-monomer in the formulation than the Fuji Xerox latex. The latex aggregation is carried out in the range of pH between 7 and 9 in a medium that is mostly aqueous but with significant soluble organic (alcohol) content. The preferred coagulant appears to be based on the use of the calcium ion (Ca^{++}). K-M has generally favored a polypropylene wax as the release agent. This material has a higher melt point than the polyethylene wax use originally by Fuji Xerox. Some of these distinguishing features are outlined in the first US patent issued to Konica in December 1997 [10]. Particle stabilization (by increasing the pH of the aggregate slurry to ~11) during coalescence is not always practiced and K-M have patents describing the dilution of the coalescing dispersion using the addition of a salt solution [11]. The K-M process may also be used to form core-shell toner particles.

Konica-Minolta use latex aggregate CPT technology in all their current monochrome and color EP products and have recently released an improved version of the toner, the Simitri™ HD material.

Mitsubishi Chemical, Matsushita and FujiFilm aggregated CPT.

Mitsubishi Chemical manufactures latex aggregated CPT particles. These base particles are employed by OEM print engine suppliers and vendors of aftermarket supplies. The technology used in these products, at least as described in the US patents issued to Mitsubishi Chemical [12], appears similar to that used by Fuji Xerox. The favored coagulant for the latex is, however, the aluminum ion (Al^{+++}) in the form of aluminum sulfate.

Matsushita claims the use of latex aggregated toners in the product releases for a series of EP products. As of late May 2007 no US patent has been issued to Matsushita for their process but there are at least two US patent applications that have been published concerning a latex aggregation process [13].

FujiFilm (formerly Avecia and Zeneca) also manufacture aggregated CPT particles at a commercial scale. The process used differs from the other aggregation schemes in that pH changes alone are employed; first to aggregate and then to stabilize the particles in a coalescence stage. The process depends on starting with latex that has a weakly acid functionalized surface. This latex is negatively charged when suspended in water at a pH of ~10 and has almost no charge at a pH of less than 4. In a low pH environment the latex suspension is unstable (coagulates) as the electrostatic repulsion is minimal at this pH. Using this latex the toner formation procedure for making toner sized particles from a blend of the latex and dispersions of colorant and wax is outlined in a US patent issued to Avecia in 2003 [14]. Some of the technical aspects and the colloid chemistry of this aggregation/ coalescence process are illustrated by the model system studies reported in two papers published in 2005 by Ding *et.al.* [15]. The process involves first blending latex, colorant and wax dispersions together at a high pH (at least 9) and then aggregating the system by lowering the pH below 4. The gelled material that forms is sheared and heated above the T(g) of the latex. The particles of toner size that are formed are stabilized by increasing the pH of the slurry to a value ~7 and the aggregates are coalesced into compact particles under these conditions. There appears to be no obvious means to modify the FujiFilm process to produce a toner with a core-shell structure using the same latex that forms the core of the particle.

The near future of aggregated CPT technology

All CPT resin materials currently in production are based on styrene and butyl acrylate monomers with a small carboxylic acid component. Examination of the recent patent literature shows that considerable effort is being devoted to making an aggregated toner starting from a dispersion of polyester. Many different approaches are being explored to make polyester particles that are smaller than 500 nm. Polyester resins are favored by many in the EP materials community and had in recent years displaced styrene resins in conventional toner applications. This trend has been reversed by many of the initial CPT designs but the polyester tradition continues with chemical toners from Ricoh – see above. It is of interest to speculate on what factors are stopping polyester from breaking into the aggregated CPT commercialization. Polyester resin is known to provide a sound resin base for low melt color toners. The resin shows good fix behavior but the drawbacks today might lie in the relative cost of the resin in comparison to latex made by emulsion polymerization and in the sensitivity of polyester to changes in environmental conditions, particularly in high relative humidity, RH, sensitivity.

References

[1] U.S. Patent # 4,797,339, "*Toner for developing electrostatic image*" Issued to Nippon Carbide K.K.K. January 10, 1989.

[2] U.S. Patent # 4,996,127, "*Toner for developing an electrostatically charged image*" Issued to Nippon Carbide K.K.K. February 26, 1991.

[3] U.S. Patent # 5,344,738, "*Process of making toner compositions*" Issued to Xerox Corporation September 6, 1994.

[4] (a) L. Lazar and S.A.M. Hesp, "*Controlled aggregation of polymer lattices. Part 1: Synthesis and characterization of a model system*". Particulate Science and Technology, **18**, 103 (2000).
(b) L. Lazar and S.A.M. Hesp, "*Controlled aggregation of polymer lattices. Part 2: Mechanism and hydrodynamics of the process*". Particulate Science and Technology, **18**, 121 (2000).
(c) L. Lazar and S.A.M. Hesp, "*Controlled aggregation of polymer lattices. Part 2: Influence of temperature and surface chemistry*". Particulate Science and Technology, **18**, 143 (2000).

[5] U.S. Patent # 5,849,456, "*Toner for developing electrostatic charge image, production method thereof, and image formation method*". Issued to Fuji Xerox Co., December 15, 1998.

[6] U.S. Patent # 6,153,346, "*Electrostatic imaging development toner, process for the production thereof, electrostatic image developer and process for the formation of image*". Issued to Fuji Xerox Co., November 28, 2000.

[7] U.S. Patent # 6,329,114, "*Electrostatic imaging development toner, production method thereof, electrostatic image developer and image-forming process*". Issued to Fuji Xerox Co., December 11, 2001.

[8] E.P. Otocka, M.Y. Hellman and L.L. Blyler, "*Terminal-group association in carboxy- and carboxylate-terminated polybutadiene*" J. Applied Physics, **40**, 4221 (1969).

[9] U.S. Patent # 6,733,944, "*Image forming process*". Issued to Fuji Xerox Co., May 11, 2004.

[10] U.S. Patent # 5,702,860, "Method for producing non-spherical particle". Issued to Konica Corp., December 30, 1997.

[11] U.S. Patent # 6,821,695, "*Electrostatic latent image developing toner and production method thereof*". Issued to Konica Corp., November 23, 2004.

[12] U.S. Patent # 6,500,596, "*Method for producing an electrostatic image developing toner*". Issued to Mitsubishi Chemical Corp., December 31, 2002.

[13] (a) US Patent Application # 2005/0196694, "*Toner, method for producing toner, two component developer, and image forming apparatus*". Published September 8, 2005, assigned to Matsushita.
(b) US Patent Application # 2006/0147828, "*Toner, process for producing the same, two-component developing agent and method of image formation*". Published July 6, 2006, assigned to Matsushita.

[14] U.S. Patent # 6,531,254, "*Process for making particulate compositions*". Issued to Avecia Ltd., March 11, 2003.

[15] (a) P. Ding, A.W. Pacek, K. Abinhava, S. Pickard, M.R. Edwards and A.W. Nienow, "*A process for the manufacture of chemically produced toner (CPT). I. Evolution of structure and rheology*". Ind. Eng. Chem. Res. **44**, 6004 (2005).
(b) P. Ding, A.W. Pacek, K. Abinhava, S. Pickard, M.R. Edwards and A.W. Nienow, "*A process for the manufacture of chemically produced toner (CPT). II. Effect of operating conditions*". Ind. Eng. Chem. Res. **44**, 6004 (2005).

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Mike Hopper is the inventor of 60 US patents and worked on chemical toner technology for the last 10 years of his 30 year tenure as a scientist at the Xerox Research Centre of Canada. He retired from Xerox in 2004 and is currently active as a consultant in the field of the forensic examination of documents and works of art. He completed post-graduate studies in physical chemistry at the University of Natal, South Africa and is a member of the AIC and FSCT.