Polyester-Based Chemically Prepared Toner for High-Speed Digital Production Printing

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Abstract

Recently, chemically prepared toners (CPTs) have been finding their way into an increasing number of electrophotographic printers. Although all these printers claim to utilize CPT as marking particles, the toner composition and manufacturing method used can be very different from each other. The production of conventional melt pulverized toners (MPTs) essentially consists of melt compounding and a pulverization operation of toner ingredients using standard equipment and processes that are similar for most suppliers. Different CPT manufacturers, on the other hand, produce the chemically prepared toners via entirely different approaches. The chemical methods of manufacturing include: suspension polymerization, emulsion aggregation, solvent dispersion, and the like. Each method used in the production of chemically prepared toner has its associated limitations and advantages.

Use of polyester as the toner polymer is often desired because of the inherent advantages offered by these resins over styrene-acrylate copolymers. Polyester binders provide a unique melt flow and mechanical toughness that is highly desirable in high-speed digital printing applications. These resins are also more suited for digital printing because of their charging behavior.

The CPT process developed at Eastman Kodak Company offers the flexibility of using any soluble polymer as a toner resin or the use of monomers that are suitable for additional polymerization for making linear or crosslinked toners. With this solvent-based process, it is possible to prepare chemical toners that are based on polyester binders, which are uniquely desired in production printing. This manufacturing process is suitable for making chemically prepared toners that have the narrowest particle size distribution in the industry. Shape control is very extensive using this approach, and particle shapes ranging from completely spherical to raisin-like can be prepared easily. The degree of irregularity can be controlled to produce particles that provide optimum performance in the machine. There is a considerable amount of flexibility offered by this solvent-based process. Toner ingredients that are affected or changed by elevated temperatures can be easily incorporated into toners because this toner manufacturing process does not require any heating. This process can be used to tailor-make toners that simplify the equipment design and electrophotographic process to provide a consistent performance in producing high image quality and lower costs for printing.

Introduction

Until recently, all toners were produced by the conventional melt compounding of ingredients in an extruder. The resulting material was then pulverized and classified prior to surface treatment. A schematic of the process used in the manufacture of Melt Pulverized Toners (MPT) is shown below in Figure 1.

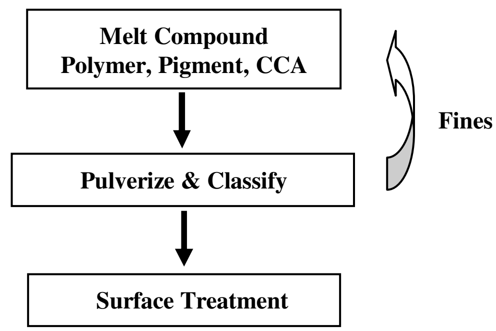


Figure 1. *Conventional Manufacturing Process for Melt Pulverized Toners.*

Although the conventional MPT process is not very energy-efficient, it is quite well understood and, as a consequence, practiced widely. The grinding properties and toner yield are strongly affected by the resin polymer selection. For any choice of resin, the energy required for pulverization increases in proportion to the amount of surface area created [1]. This implies that as smaller particle size toners are desired for improved image quality, more mechanical energy is necessary for grinding. Furthermore, as smaller particles are pursued, the amount of even smaller particles, or fines, generated in the pulverization step increases. Although these fines can be completely recycled by feeding them back to the extruder or roll mill, the conventional mechanical process becomes inefficient when pursuing smaller particles. The grinding rates also decrease for smaller toner particles, but the biggest challenge comes at the classification step. For smaller toner particles, not only do the classification rates slow, but the classification efficiency also decreases. For making toner particles of an average diameter of 5 µm or less, typical overall volume yields are only 50% based on the extruder output.

The incorporation of toner additives is, however, quite simple in the melt pulverization process. As long as the toner ingredients either melt or are dispersed and distributed during the shearing action produced during the compounding step, a uniform composition is typically achieved. For harder to disperse toner components, such as waxes, many different approaches have been developed and practiced in the industry [2].

Chemically Prepared Toners

In recent years, there has been a noticeable shift in the manufacture and use of toners manufactured by non-conventional methods. The trends [3] for production of toners by both melt pulverization and chemical process are shown in Figure 2. Production of conventional ground toners is still increasing at a reasonably healthy pace, but the gains for the CPT sector have been quite spectacular.

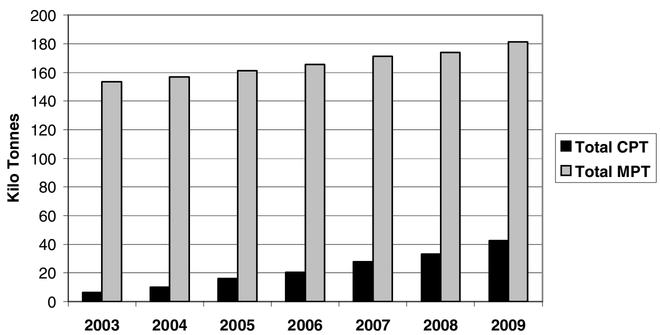


Figure 2. *Worldwide toner production volume forecast for various toner manufacturing processes.*

Currently ~12 percent of all the toner manufactured is produced by chemical means. Within the CPT sector, the majority of the toners produced are black only, while only one-third of the total CPT toners produced are for color application.

Although the term "CPT" is used to describe all toners other than melt pulverized toners, there are a multitude of manufacturing processes that are used to make such toners. A list of various CPT manufacturing processes is listed in Table I along with the types of polymers used [4].

TABLE I: Various types of CPT processes and binder choice

CPT	Resin Pzn Method	Toner Binder
Suspension	Suspension	Styrene-Acrylate
Emulsion Aggregation (EA)	Emulsion	Styrene-Acrylate
Encapsulation	Suspension/Emulsion Step Growth	Styrene-Acrylate, Polyester
PxP	Step Growth	Polyester
Dispersion Pzn	Step Growth*	Polyester
Precipitation	Step Growth*	Polyester
Solvent Dispersion	Step Growth*	Polyester
Chemical Milling	Step Growth*	Polyester

*Pre-Formed Polyester

CPT technology offers several advantages over the conventional MPT technology [5]. Some of the advantages are:

- Small particle size
- Narrow size distribution
- Various toner shapes with wide and controllable range of toner circularity surface roughness
- Good pigment dispersion
- High wax loading and uniform dispersion
- Uniformity of composition
- Core-shell technology possible
- Surface chemistry control

However, toners prepared by chemical means are typically more difficult to recycle, and any residual surfactant/dispersants can adversely affect the toner charge and its environmental charge stability

Of the various types of chemical toners commercially available today, the emulsion aggregation and suspension polymerization types are most common [6]. As a consequence, CPT continues to be predominantly based on the styrene-acrylate type of binder resins. Such toners have a much higher melt viscosity for a number of reasons. In most cases, this is not a serious limitation because of the equipment such toners are selected for. Most of these toners are used in relatively slow-speed desktop color printers and monochrome applications.

For high-speed color printers, polyester would be much better-suited than styrene-acrylate polymers because of their superior mechanical toughness at low molecular weights. It is possible to produce low-melt viscosity toners without having to use a very brittle polymer binder that can cause a negative impact on developer life and image permanence. Although polyesters can be crosslinked, there are limitations on how they can be used in some CPT processes. Because polyesters cannot be polymerized by addition polymerization methods, EA and suspension-based polyester CPTs are not possible. Most CPT manufacturing techniques that can use polyesters involve the use of solvent or plasticizers. There is work being done to make polyester dispersions by mechanical and/or chemical means, to produce polyester-based CPTs without using solvents.

The majority of the polyester resins that are in the toner industry are predominantly based on bis-phenol A. These polymers are preferred over the non-bis-phenol A containing polyesters despite the higher cost for bis-phenol A monomer. In general, the non-bis-phenol based polyesters are less expensive but are highly brittle. Their use is typically limited to powder coatings. With CPT processes, the fragile nature of this binder should not be a major factor. However, another problem that is encountered with non-bis A polyesters is the poor charging behavior in toners. Part of the problems lies in the fact that these resins are typically produced for the coating industry and often contain anti-stat additives.

Styrene-acrylate copolymers are generally less expensive than polyester resins, but the manufacturing cost of toners based on different CPT processes is still quite similar regardless of the binder polymer used. Advances are continuously being made in the CPT manufacturing processes, and as a consequence, the price difference between CPT and MPT manufacturing is slowly shrinking.

Kodak's CPT Process

The method of producing toners by chemical means developed at Kodak offers incredible flexibility in toner polymer selection, and at the same time enhances the attributes of the CPT particles. In this process [7], [8], [9], a water-immiscible organic phase is sheared to form small droplets suspended in an aqueous medium containing a water dispersible water-insoluble solid colloid as the suspension stabilizer. Toner particles are grown from a submicron size to the desired final size till a uniform and narrow particle size is produced.

Because of this behavior, this process is also referred to as the "Limited Coalescence" (LC) process. In general, this process can be classified into two categories:

- Polymerization LC Method
- Evaporative LC Method

In the polymerization LC method, the organic phase comprises a mixture of polymerizable vinyl monomers in which toner ingredients are dispersed or dissolved, in addition to a free radical initiator. After homogenization with the aqueous phase containing particulate stabilizer, the mixture is heated to initiate polymerization. After polymerization is completed, the particles are isolated from the aqueous phase and dried. This process provides the toner particles with extremely narrow size distribution, as depicted in Figure 3.

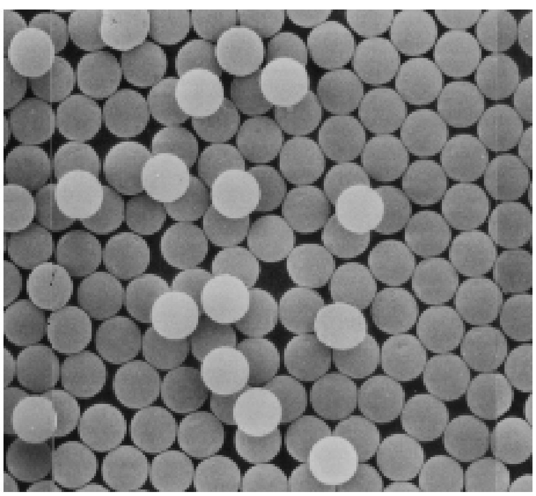


Figure 3. *Scan electron micrograph of toner particles produced by Limited Coalescence process.*

Evaporative LC is the second example of a process that results in polymer particles that have a narrow size distribution using a solid colloidal stabilizer. It comprises forming a solution of polymer in a solvent that is immiscible with water, dispersing the polymer/solvent solution in an aqueous medium containing a solid colloidal stabilizer, removing the solvent, and dehydrating and drying the resulting particles. Initially, the stabilized organic phase also contains the solvent. As the solvent is removed, the size of the particles is reduced. The final particle size of the toner can be predicted by the following expression:

$$R_{Final} = 3 \times (\text{Wt. Fraction of Polymer dissolved})^{1/3} \times R_{Initial}$$

where $R_{Initial}$ is the initial particle size with solvent and R_{Final} is the final size of the resulting toner.

Control of Size

Kodak's process uses a particulate stabilizer to produce toner particles. The function of the particulate stabilizer is to control the agglomeration of the particles during growth and to control the growth once the final particle size has been achieved. The colloid performs this function by adhering to the droplets at the water/organic interface to form a layer on the surface of the droplets. After the organic phase droplets have coalesced with other droplets and have grown to a particular diameter, the presence of the layer of colloidal stabilizer particles on the surface of the droplets prevents them from further coalescing and increasing in diameter. In this way, all of the droplets tend to grow to approximately the same diameter, so that the resulting toner particles have a narrow size distribution. The concentration and size of the colloid determines the size of the droplets. The dependence of toner particle size and the amount of stabilizer is illustrated in Figure 4.

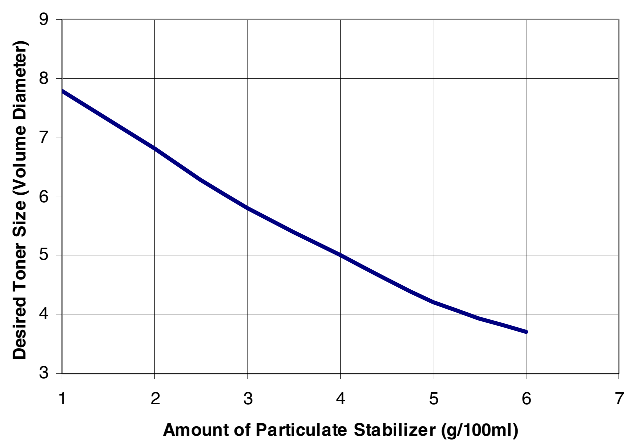


Figure 4. *Relationship between amount of particulate stabilizer and resulting toner particle size produced by Limited Coalescence method.*

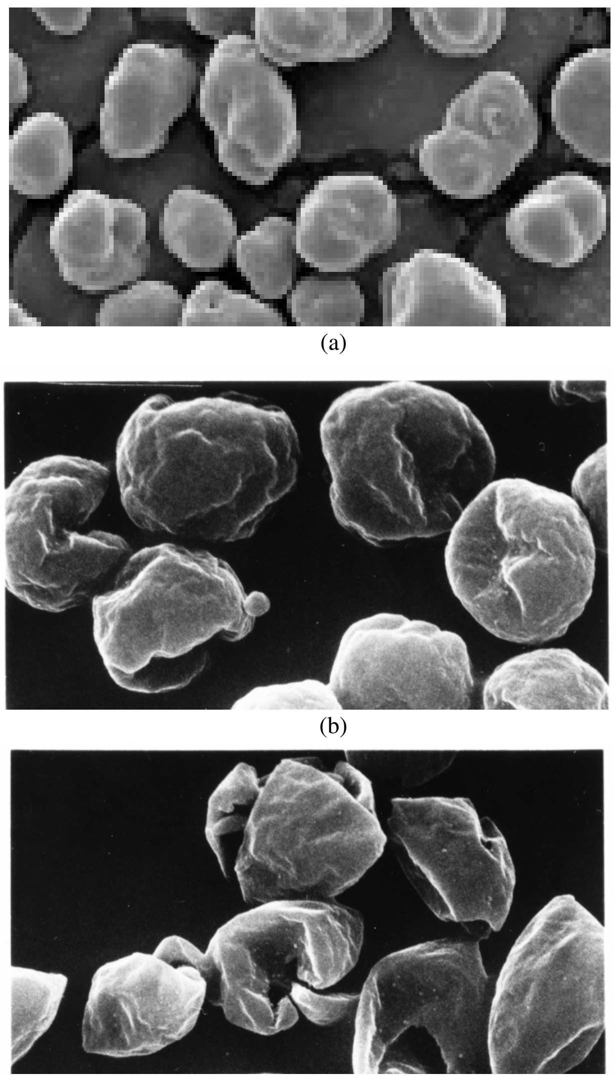
The amount of stabilizer needed for the desired particle size would obviously depend on both the concentration of the stabilizer in its solution as well the particle size of the stabilizer. The overall relationship shown above, however, is still maintained. As the particle size of the stabilizer decreases, less of it is required to produce a given toner size. Particulate suspension stabilizers employed in the preparation of polymers include polymer latex, silica, alumina, barium sulfate, calcium sulfate, barium carbonate, calcium, carbonate calcium phosphate, and the like.

Control of Shape

The control of shape is important for various reasons, including:

- Cleaning
- Developer flow
- Transfer efficiency
- Image quality
- Manufacturing ease

The Limited Coalescence method developed at Kodak offers the means of controlling the shape of the particle. Not only can irregular shapes be consistently produced, but the degree of roughness can also be controlled to provide optimum toner performance in the electrophotographic system. Shape can be controlled in both the polymerization as well as the evaporative methods. There are a number of approaches in which it is possible to control the shape of the toner particles. Typically, controlling the solution elasticity at the interface during the formation of the particles can control their shape. Alternatively, a shear force can be applied to the organic/aqueous phase mixture during the formation of the toner particles.



(a) (b) (c)

Figure 5. *Scan electron micrograph of various non-spherical toner particles that can also be produced by a Limited Coalescence process.*

Additional Features of LC Process

With the polymerization LC method, both linear and crosslinked toner polymers can be synthesized. Typically, polymer chain transfer and/or crosslinking agents can be added to the organic phase, prior to the homogenization with the aqueous phase, to control the desired molecular architecture and rheological response. For evaporation LC, the solution viscosity is the most critical parameter. The method is applicable to only those starting polymers, which can be dissolved in the solvent. Polymer molecular weight and percent solids in the preferred solution dictate the solution viscosity. It is possible to incorporate a molecular weight extender, which would increase the viscosity once the solvent has been removed.

Kodak's LC process to manufacture CPTs is a continuous process that is very economical and does not require large holding tanks. In the solution-based evaporative LC process, all the solvent and water are recycled, making it environmentally friendly.

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Author Biography

Dr. Dinesh Tyagi received his Ph.D. degree from Virginia Tech in 1985 from the Department of Chemical Engineering with a thesis entitled "Structure-Property Relationships in Segmented Polymers." After one year in a post-doctoral position there, he joined Eastman Kodak Company as a Research Scientist where he started worked in the toner development area. He was promoted to Senior Research Scientist in 1989, and in 1993 he was appointed Research Associate. The following year, he was inducted into Kodak's Distinguished Inventors Gallery. In 1999, he joined NexPress Solutions, which was later absorbed into Kodak. He has continued to work in the area of toners and electrophotography through most of his professional career. Dr. Tyagi has over 80 patents worldwide.