Chemically Prepared Toner (CPT)

A little History

Research into the creation of toner directly by chemical means has been investigated for at least 30 years. The methods investigated include Suspension, Dispersion and Emulsion

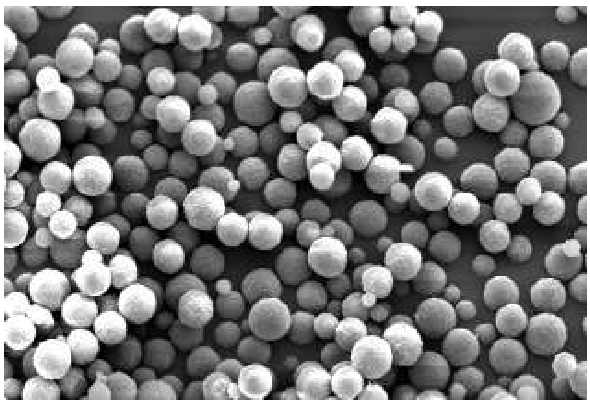


Figure 1 Chemically Prepared Toner

ploymerization, latex or emulsion aggregation and in the case of microencapsulated types, interfacial polymerizations of various types.

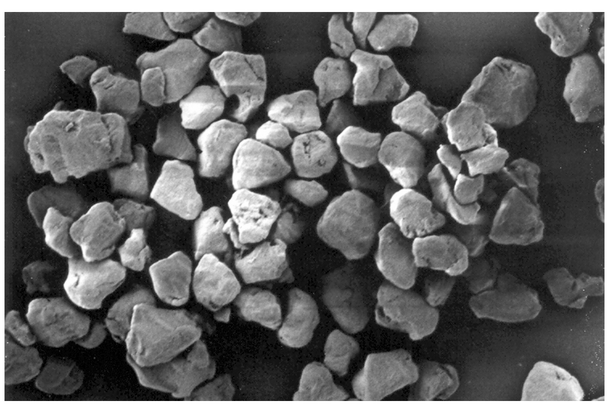


Figure 2 Conventional Toner

Xerox conducted the earliest work known in the early to mid 60's. The work focused on the production of toners by "in-situ" polymerization methods. The work was ended after the expenditure of several millions of dollars up to the late 60's. Subsequently, research work was conducted by many companies in the field, including Reprographic Materials Inc., Casco-Nobel, Surface Processes Corporation, 3M, Synfax and Nippon Paint. Since 1990 the list has grown to include Xerox/Fuji Xerox/Nippon Carbide, Zeon Corporation, Canon, Minolta, Konica, Ricoh, Mitsubishi, Dainippon Ink and Chemicals, TDK, Eastman Kodak, Kao, Nippon Shokubai, Toshiba, Tomoegawa, Toyo, Samsung, Fujitsu, Kyocera Mita, DPI Solutions and Seiko Epson. Work on the creation of particulate polymer of controlled size can be traced back to the 1930’s through patents granted including that of Crawford et al. of ICI Patent # 2,108,044 of February 1938.

Chemically prepared toners has been referred to by a variety of names like chemically prepared toner, chemically produced toner, chemical toner, polymerized toner, polymer toner, in-situ polymerized toner, suspension polymerized toner, emulsion polymerized toner, emulsion aggregation toner, controlled agglomeration, capsule toner, microcapsule toner, encapsulated toner, microencapsulation toner, microencapsulated toner and the list goes on! There are many different types of CPT. Most methods of manufacture are proprietary to their inventors and manufacturers and are covered by an enormous raft of patents worldwide.

Why So Long Before Commercialization?

If the advantages in the use of CPT are so important, why hasn’t the technology been used until now? There are a variety of reasons for this. Firstly, toner based printing systems, until recently, have not been ready to take advantage of the benefits and capabilities of chemical toner. The subsystems in print engines for latent image creation, development, transfer and fixing had not been developed to such a level of efficiency or quality to make a sufficiently noticeable difference in print quality with better toners. Recent developments in these subsystems have made the difference in toner performance now more meaningful.

Major hardware manufacturers have lacked the capability and the facilities to use CPT processes. Toner development often requires the simultaneous co-development of both hardware and toner materials. This has meant that, to develop CPT, the hardware manufacturers have had to develop such toner technology before being able to implement this in hardware. A further roadblock is presented by the technological and IP challenges in the development of CPT technology.

In addition the “toner industry” has significant investment in conventional toner manufacturing equipment and much manufacturing plant currently in place has significant useful operational life. The investment required for the manufacture CPT would impose an additional burden on capital investment. Environmental benefits of the switch from conventional toners to Chemically Prepared Toners have not been mandated and consciousness of the benefits of environmental improvements has not been at the forefront of industry awareness. Recent legislation has highlighted the potential contribution CPT manufacturing has toward improvements in pollutant emission reduction.

Why Chemically Prepared Toner Anyway?

In toner based printing, for optimum print quality, the toner materials need to be improved in a variety of ways. There is the need for small mean particle size, narrow particle size distribution, narrow charge distribution, low energy fixing (particularly for color applications) and predictability of toner development behavior.

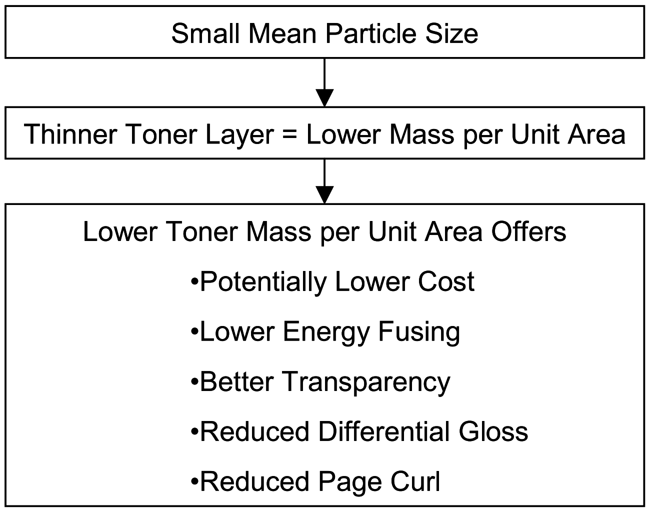
CPT can help to achieve these goals. The features of CPT technologies include:

- Easier manufacture of small size toner
- Control of particle size to make much narrow particle size distribution
- Homogenous toner composition leading to narrower charge distribution
- Control of toner particle shape giving improved toner properties
- Molecular weight composition tuning improving melt (fixing) properties and enabling low energy oilless fixing

Why Do We Need Small Size Toner?

We need to ask the question, how small does the toner have to be to achieve good quality reproduction? Grunlach's Law theoretically shows that there is an inverse exponential relationship between the mean toner particle size and addressed dot density in digital printing. Theoretically, for perfect reproduction of dots and print features at 600 dpi a mean particle size of about 5μ is required and at 1200 dpi you need a toner of about 3μ. It is a matter of opinion what the lowest mean particle size achievable economically with the conventional toner manufacturing process would be but many experts say that the limit is about 7μ. It is certain however that, under no conditions currently known, conventional manufacturing is economically capable of producing toner at the 3 μ level.

In addition to being able to resolve small print features, there are other benefits from the use of small particle size toner. The smaller the mean particle size of the toner used to form an image is, the thinner the toner layer is in the image areas. This then means that the amount of toner, the toner transferred mass per unit area (TMA), is lower for such a toner. The benefits of this feature are shown in the diagram below.



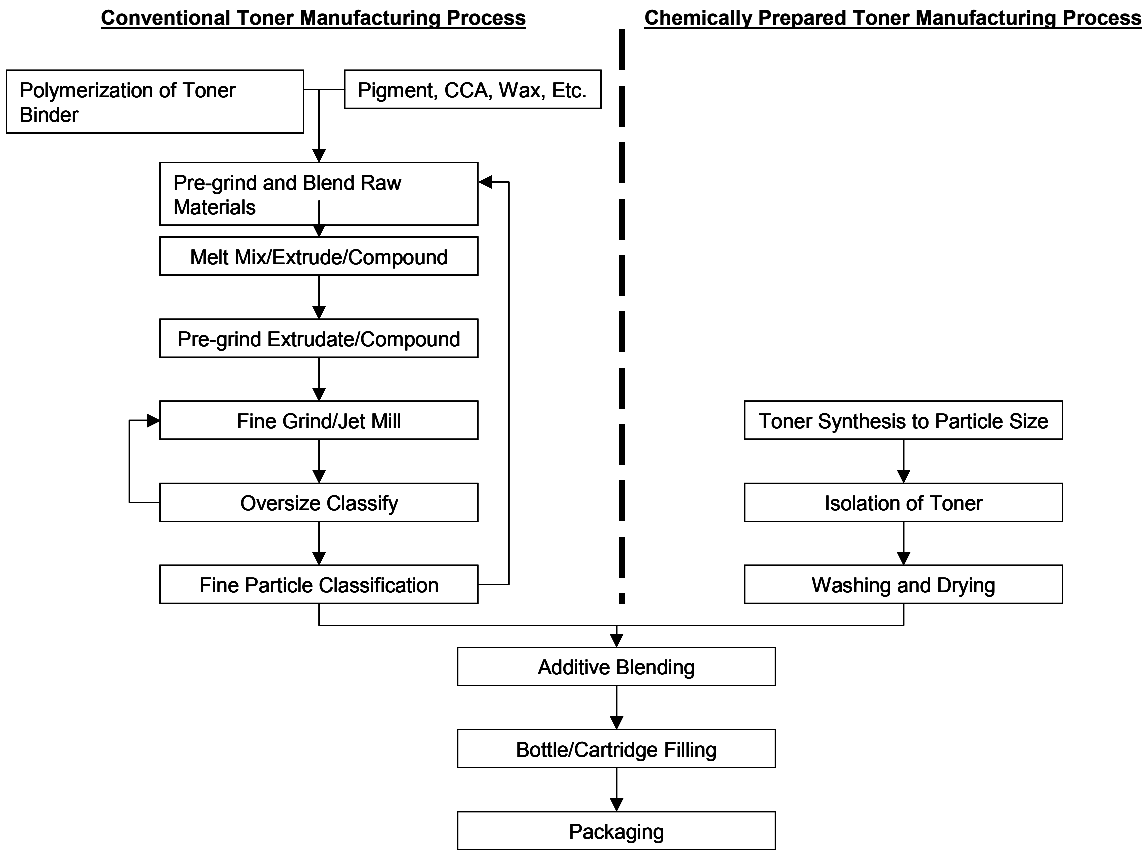
At the same time as making smaller toner particles, CPT processes can be manipulated to produce narrower particle size distribution toner. This in combination with the ability to achieve homogeneity of composition within a toner particle and from between particles that enables the achievement of narrower particle charge distribution which helps to achieve better print quality. Conventional manufacturing does not achieve a high degree of uniformity or homogeneity. In conventional toner manufacture, the relatively poor distribution of bulk and surface additives as well as uneven size uniformity, translates into non-homogeneous electrostatic charge behavior that, amongst other factors, leads to performance defects and limitations with conventional toner. I particular, the mono-component development process demands rapid and uniform charging of toner. The improvements achievable with CPT can be taken advantage of to the fullest extent by this type of print process.

Shape control also plays a part in improving the predictability of charging homogeneity in toner. Similarly shaped toner particles behave in similar ways. The more homgenous a toner is in size shape and composition the more predictable the toner will be in performance. The more predictable the toner is in performance the better the print quality will be.

Conventional and Chemical Toner Manufacturing Methods Compared

The simplicity that typifies chemically prepared toner manufacture compared to conventional manufacturing is shown below.

The two processes become common at the additive blending step. The toner manufacturer does



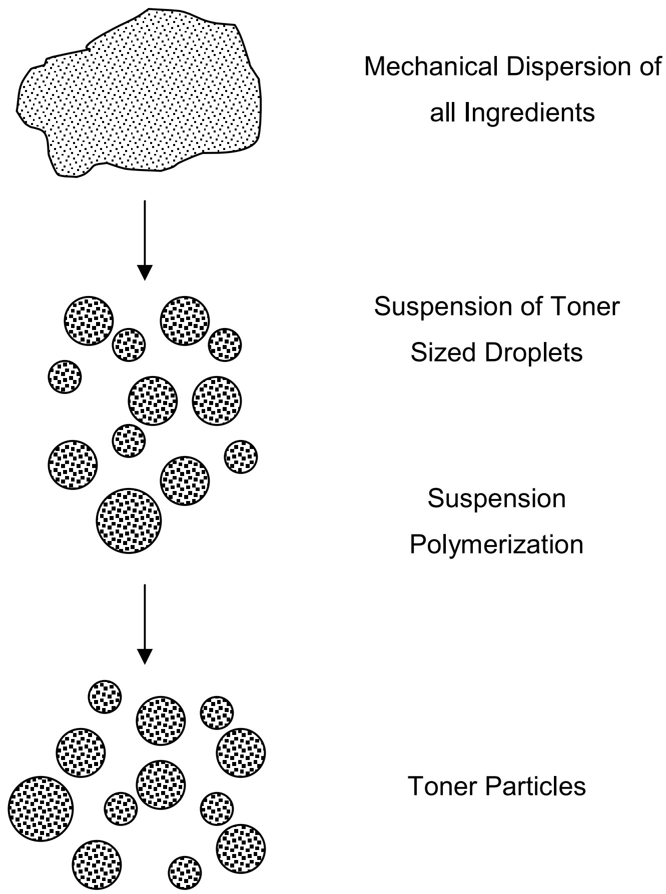
not usually perform polymerization of toner binder resin used in conventional toners though there are some exceptions to this. Nevertheless, resin polymerization is a necessary part of the overall conventional manufacturing process. On the other hand, the "toner synthesis step in the process flow diagram for chemically prepared toners, is not necessarily a single step and indeed in many cases this process includes multiple steps, and can alter the apparent simplicity of CPT significantly.

Chemically Prepared Toner Basics

What is meant by CPT is, of course, fine particulate toner prepared by synthesis. There are some basic types of CPT manufacturing method – suspension polymerization, emulsion/latex aggregation, chemical milling and Polyester (Elongation) Polymerization (PXP).

Suspension Polymerization

Diagrammatically the process is as shown in the diagram below. Chemically, the process is a free radical polymerization process. The chemistry of the other non-polymerizable ingredients, in particular the pigments used, can have a significant affect on the resulting product. Different pigments, carbon black, quinacridone, phthalocyanine, etc., all have different affects on free radical polymerization. Indeed different pigments in the same class differ in their affects on the process. Incorrect pigment selection can lead to the inhibition of polymerization and in there being residual unreacted monomer in the finished toner.



The polymerization is conducted at an elevated temperature and for a specific time with agitation at a specific rate. These conditions vary according to the formulation and the specification of the toner being produced. Once polymerization is complete the material is the washed, filtered and dried. The dried CPT is then blended with extra-particulate additives such as silica. A commercial example of the use of this technology is by Zeon Corporation.

Emulsion ploymerization/latex aggregation

Emulsion polymerization is a method in which, in an emulsion, monomers are diffused into what is referred to as a micelle where free radical polymerization proceeds. There is a resulting formation of polymer particles by this process. The other necessary components of toner – pigment, charge control agent, wax, etc. – cannot internalized into the polymer particles because such materials cannot diffuse into the micelle. The method offers the opportunity to separate the pigmentation and polymerization steps and means that there is no interference by these ingredients with the polymerization process. The toner particle formation step in the process is more dependent upon the chemistry of processing rather than mechanical factors and thereby it is claimed that the particle size and particle size distribution is therefore more controllable than suspension polymerization.

The process outline is shown below. The manufacturing method for toner is from the two

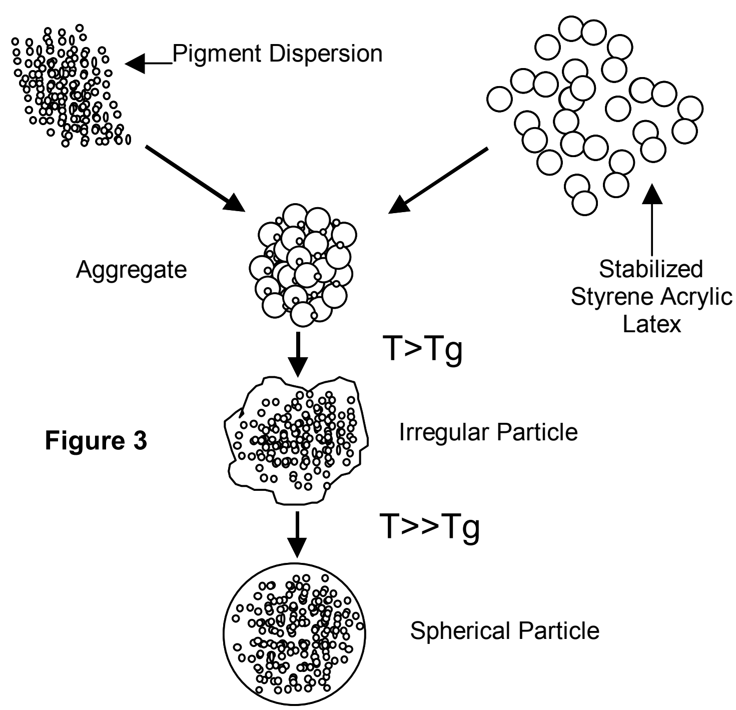


Figure 3

separate parts. These two parts are then mixed at elevated temperature in a low intensity mixer for a given number of hours. In this process the “Primary particles” in the form of a stabilized styrene acrylic latex are formed. These non-pigmented emulsion polymerized particles are between 0.1 - 0.3 microns in size. The colorant and/or magnetite and CCA is added to the primary particles in their aqueous medium. Secondary particles are formed by the agglomeration of the solids in the aqueous medium. These secondary particles contain the primary particles, the pigment/magnetite and CCA. The secondary particles are 1.0 - 4.0 microns size at this stage of production. The secondary particles agglomerate further to form “associated particles” with a size range of 5.0 - 13.0μ. Shape adjustment is conducted by control of the temperature and other conditions. Increasing the temperature to above, what is called, the glass transition temperature (Tg) controls the viscosity of the heated polymer and allows interfacial forces and surface tension to be used to change the particle shape. The shape can be changed from completely irregular to perfectly spherical shape. The mix is then filtered washed and dried yielding a pre toner ready for blending with silica as a flow and charging additive.

Examples of the use of this technology are Xerox, Fuji Xerox and Konica Minolta.

Polyester (Elongation) Polymerization (PxP)

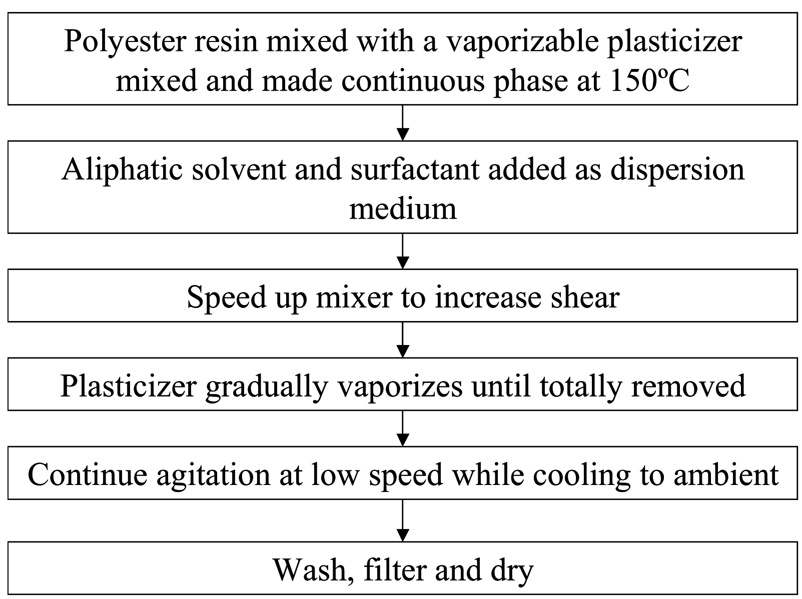
Condensation Polymerization can be performed basically in two different modes Single phase (bulk) polymerization or 2 Phase (interfacial polycondensation). With this type, so far, it has not been able to polymerize particles directly to size, so the technique has not been used alone. Typical of the materials produced are polyesters. However, in a modified method, Ricoh has claimed success in the production of what they call their Polyester (Elongation) Polymerization (PxP) Toner process. In this process partially reacted materials called oligomers, plus other toner components are combined in a dispersing medium to prepare toner size droplets. The reaction of the materials is then completed and toner is finished by washing, filtration and drying .

Ricoh claims excellent powder flowability, developability and transfer efficiency with small, narrow particle size distribution, excellent gloss and superior hot offset resistance when used for colored toner. They can also make oiless fixing toners by this method. The toner used by Ricoh commercially is sub-contract manufactured by Sanyo Chemical.

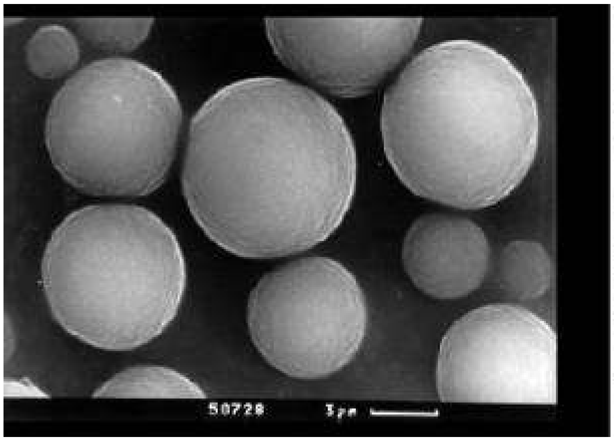
Chemical Milling

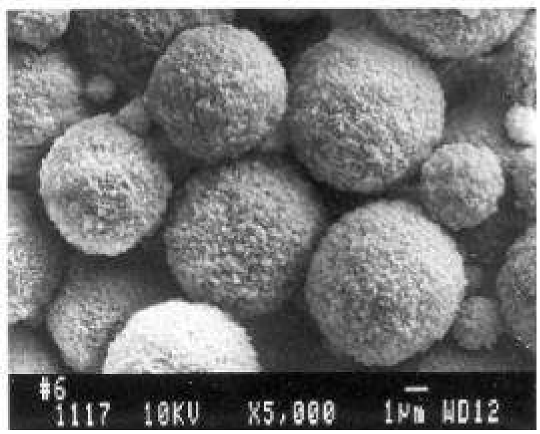
Chemical Milling is a process developed by a company called DPI Solutions from Korea. There are no polymerization steps involved in this production technology. The technique is capable of using any commercially available toner resin though the preferred type would appear to be polyester. Control of the process means that small toner of narrow particle size distribution may be produced. The particles are spheroidal and it is a feature of the process that there is the capability to control surface morphology. The degree of rough/micro-serrated texture is controllable thereby enabling the control of, amongst other parameters, charging speed and flowabilty. The production equipment for the process is relatively simple and low in capital cost. The process also is relatively low in specific energy content. It is possible to use pigments or dyes as the colorant. With this toner it is possible to achieve maximum color value and hence large color gamut, and also achieve good color permanence and low bleed characteristics. The raw materials used in the process are also less dangerous for handling than those in polymerized CPT technologies.

The Figure below gives an overview of the production method.



The SEMs below show two samples of toners representing different surface morphologies possible by this technology. The one on the left has a very smooth surface and the tone on the right has a micro-serrated surface.





Microencapsulation

Many CPT products are microencapsulated or encapsulated. These terms are interchangeable. In micro-encapsulation the particles produced have a core/shell structure. The intent is that some of the properties of the particle are derived from the core and some from the shell surrounding it. The properties derived from shell are mechanical strength and thermal stability adequate to prevent attrition in any part of the filling, transportation storage or use in a print engine. The shell also controls to a great extent the tribo properties of the toner and can be manipulated to tune this property. The powder flow also depends on the shell properties in its morphology and composition.

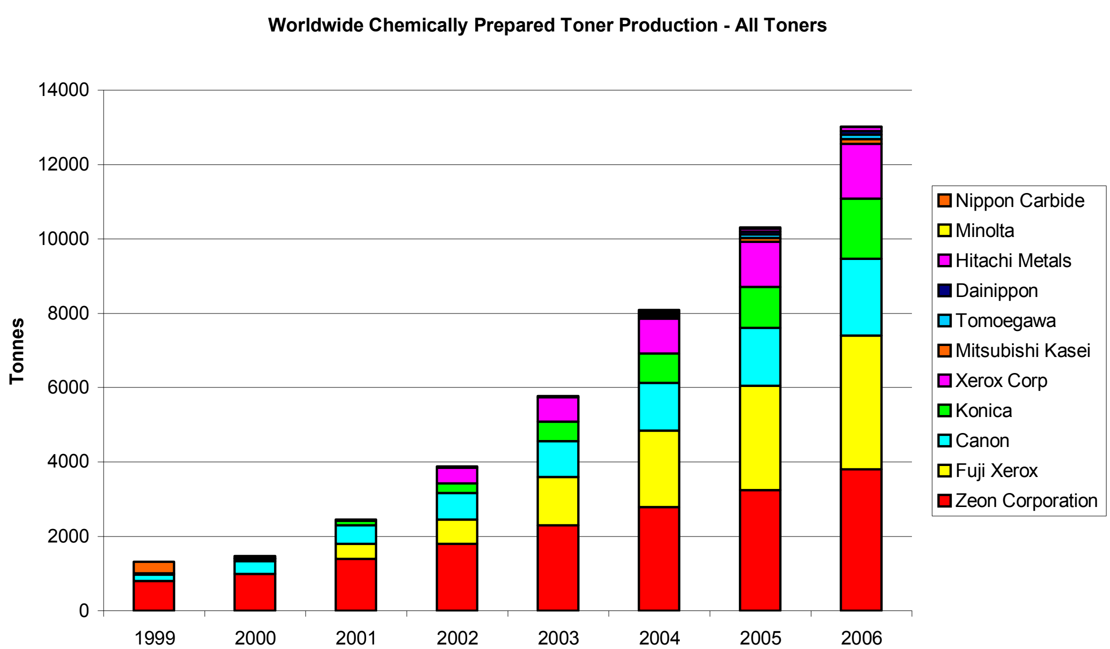
The properties derived from core include the fusing and fix properties that are determined by the melt rheologies adjusted by chemical composition and molecular weight. The core of a microencapsulated toner usually contains the colorant. The thickness of the shell or shells formed can be varied in the process giving the toner different properties.

A variety of techniques are used to achieve this kind of particle structure. There is much IP in the area and it can be said that there at least as many technologies as there are participants in R&D in the area. There are a variety of methods in use and proposed. One method is that, firstly an unpolymerized core mixture is coated with unpolymerized shell mixture. The shell is polymerized first interfacially with a shell co-monomer soluble in core monomer. The core is then thermally polymerized. Currently commercially available products are from Canon and Zeon Corporation. Canon was the first to commercialize with the toners for their Pixel L series engine.

The Market

Production volume of Chemically Prepared Toners in 2001 was about 2,450 tones, 1,900 tonnes of black and 550 tonnes colored toner (Cyan, Magenta and Yellow). This represented about 1.6% of worldwide production volume of toner of all types. In 2006 it is forecast that production will reach 13,000 tons, 6.7% of the total worldwide production volume of toner.

By 2006 in addition to Canon, Fuji Xerox and Konica/Minolta, and contract toner manufacturers Zeon Corporation, Mitsubishi Chemicals and DIC are predicted to be the main manufacturers of CPT. By 2006 about 45% of the colored toner manufactured in that year worldwide will be manufactured by chemically prepared toner methods. In 2006 the production of black chemically prepared toner will be just under 10% of all black toners. In-house toner manufacturers and contract toner manufacturers will broaden their product lines with chemically prepared toner.



Conclusions

We can see that CPT potentially offers much to the print performance of toner based print systems. For the future, colored toners appear to be the primary focus of the OEMs. Many of the traditional toner manufacturers, if we can call them that, do not possess the core competency needed to master polymerization based toner preparative methods. Does this mean that the resin makers will become toner manufacturers? If that were the case then there would be a potential for shift in the profit chain away from the toner manufacturers to resin manufacturers. To stay ahead of the game the toner manufacturers must commit to investment in technology and new production facilities that will embrace CPT.