Suspension Polymerized Toners

The first types of Chemically Prepared Toner to be developed and commercialized were produced using suspension polymerization.

Suspension polymerized toner has many advantages over conventional toners. Firstly production of this type of chemically prepared toner is much simpler than that of conventional pulverized toner. Secondly the achievement of a much narrower particle size distribution makes it possible to practically produce super fine toner with a mean particle size (d50) of 5 microns. Complete elimination of classification is a very attractive proposition for a toner manufacturer and offers some economy in production. In addition it is possible to achieve more precise control of particle size distribution by this method. Furthermore, this type of toner has higher flowability, which plays a significant roll in the use of super fine toners with notable improvements in print image and print quality. The achievement of higher transfer efficiency with this type of chemically prepared toner allowed the design cleaner-less printers though recent machines do use blade cleaning. Importantly, lower temperature fusing with encapsulated suspension polymerized toner improves fusing efficiency, reduces power consumption and enables smaller print engine design.

The Suspension Polymerization Process

Suspension polymerization is a process that has been used very commonly in resin manufacture for decades. The process is what is called a free radical polymerization process. A free radical reaction is a very fast process that takes place in a fraction of a second. In a free radical polymerization process, the formation of a polymer molecule requires initiation to occur once, and then propagation to occur thousands of times. Initiation is caused by the breakdown of an initiator to create free radicals. Propagation results from the reaction of the free radicals with the monomer to cause combination of monomer molecules. The reaction becomes terminated when the desired degree of polymerization has been achieved. Termination is conducted a variety of methods according to the product objectives.

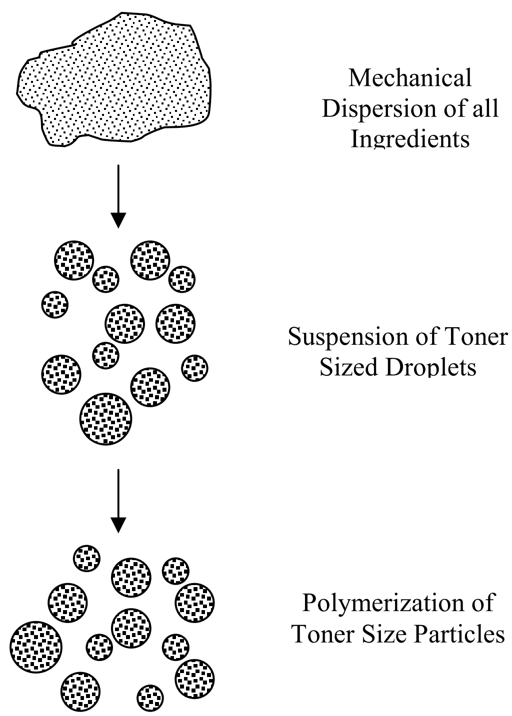
The name suspension polymerization is derived from the fact that the chain reaction process is conducted in suspension. It has some characteristics in common with the solution and emulsion polymerization processes, but those reactions are performed with the input materials in a different state.

In suspension polymerization, there are two separate input mixtures of materials or phases - the aqueous or water phase and the organic phase - that are mixed during the process to form a suspension of the organic phase in the aqueous phase. The starting point for this mixture of phases may be 10 parts of the aqueous phase and 1 part of the organic phase. The initiator used in the process is usually soluble in the organic phase. The monomers, which comprise the organic phase, are dispersed by mechanical agitation in the aqueous phase, and monomer rich droplets of the organic phase are polymerized in the shapes of the droplets. Initiation, propagation, and termination take place inside the droplet. The droplets are maintained in suspension and coalescence is prevented by the combined action of mixing and the surface-active agents used in the suspension. Mixing conditions and the surface-active agents affect the mean particle size (d50) and particle size distribution (PSD). The ability to predict and control the PSD is of prime importance in toner manufacture.

The process as described so far is as for resin manufacture but for toner manufacture other raw materials must be added to the mixtures to form toner "droplets". The chemical nature of the non-polymerizable toner ingredients, in particular the pigments used, can have a significant affect on the process. Indeed even different pigments in the same class differ in their affects on the process and incorrect pigment selection can lead to a poor finished toner.

Toner Manufacture by the Suspension Polymerization Process

Diagrammatically the basic process is as shown below.



Here one can see the two phases, an organic phase that basically contains all of the toner raw materials for the toner particles and the aqueous phase in which they are to be suspended. In the manufacturing plant quantitative feed pumps control the feed of the two phases in controlled proportions into a disperser and at a controlled rate to optimize the suspension and the formation of organic phase droplets in a disperser. The polymerization is conducted at an elevated temperature and for a specific time with agitation in the disperser 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 taken from the reactor to the washing, isolation and drying steps of the process. The dried CPT then is blended with extra-particulate additives such as silica. Schematically this is as follows:

Making Double Structure / Core Shell Toner

In double structure/core shell toner architecture, also called microencapsulated toner, the particles produced have a core surrounded by one or more shells. The intent is that some of the properties of the particle are derived from the core and some from the shell. The properties derived from shell are mechanical strength and thermal stability, adequate to prevent attrition of the toner 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 morphology and composition.

The properties derived from core include the fusing and fixing properties. These are determined by the melt rheologies of the core materials adjusted by chemical composition and molecular weight. The core of a microencapsulated toner usually contains the colorant. The cost of the toner can also be favorably affected by the choice of materials, in particular of the monomers used in the core formation. It is possible to use less expensive monomers in the core thereby reducing the raw material cost of the toner. The thickness of the shell or shells formed can be varied in the process. There are a variety of methods possible to make such toner and one method is that, firstly an unpolymerized core mixture is coated with unpolymerized shell mixture. The shell is interfacially polymerized first and the core is then polymerized using processing at an elevated temperature.

Commercial Products

There are commercial monochrome suspension polymerized toners produced for the Oki, the Toshiba/TEC fax machines manufactured by Zeon. These toners are of single structure type suspension chemically prepared toner. Zeon also produce toners for other Oki printers and are double structure / core shell type products. The table below summarizes the machine models and some toner details for commercial suspension polymerized toners.

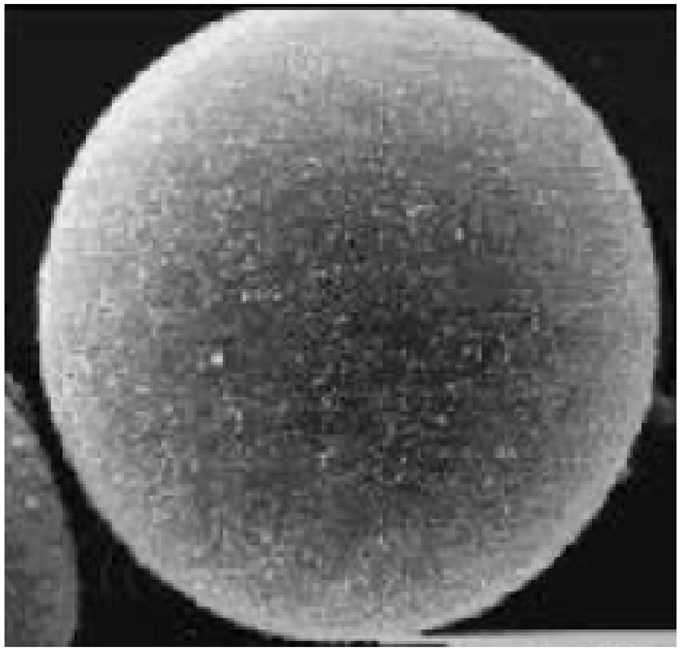
Engine Manufacturer	Model	Color	Prep. Method	Toner Manufacturer	Mean Particle Size (Vol.)
Oki	400 Series	B&W	Single Structure	Zeon Corp.	7.5µ
Toshiba/TEC	Fax	B&W	Single Structure	Zeon Corp.	7.5µ
Oki	Microline 8W, p20, ML14	B&W	Double Structure Core/Shell	Zeon Corp.	8.6µ
Brother	Brother HL1440, 1470, 1650, 1670	B&W	Double Structure Core/Shell	Zeon Corp.	8.6µ
Canon	Pixel L, CP660, LBP2040/HP4500, LBP2160/HP8500, HP8550	Cyan, Magenta, Yellow	Double Structure Core/Shell	Canon	7.5µ
Canon	IR3200, LBP2120/HP4600/HP4650/HP2500/HP1500/HP3500/HP3700/HP5500	Cyan, Magenta, Yellow, Black	Double Structure Core/Shell	Canon	Cyan, Magenta and Yellow = 7.5µ Black =8.5µ

The two manufacturers using suspension polymerization for toner manufacture are Zeon Corporation and Canon.

Zeon Corporation

Zeon Corp, formerly known as Nippon Zeon, was the first company to enter the market with commercial chemically prepared toner products. They built the world's first plant for commercial production of chemically prepared toners in Tokuyama City (Yamaguchi) and started small volume production in 1993. In 1995 their full-scale plant was commissioned and had a capacity of 1000 tonnes. They produce toner for Oki and TEC and started their production with production of spherical black mono-component toner for use in “cleanerless” engines. They increased the capacity of this plant to 1500 tonnes per annum in 1999 and commissioned new facilities in the same location in 2001 to make a total capacity 2500 tonnes per annum. Zeon commissioned their full color chemically prepared toner plant in April 2004 and expect to be producing colored toner commercially in 2005.

The following is a SEM of one toner particle of their first type of product of about 7.5 microns. This is a suspension polymerized spherical magnetic mono-component toner.



As can be seen, the CPT appears perfectly spherical which is advantageous in some respects, but does present some issues. Spherical toners represent the most uniform shape for particles and consequently offer the opportunity for the most uniform performance in charging, development and transfer. However, as is well known the cleanability by conventional methods such as blade cleaning of such particles remaining on the photoconductor after transfer presents problems.

If, as is reportedly the case, the transfer efficiency % (TE%) is very high, close to 100%, then cleanerless print architectures may be used with success. It is imperative to make TE% high to enable so-called cleanerless architecture to be successful. Because the cleanability is a major issue in application of these spherical toners, and that suspension polymerization techniques produce spherical toners, it is understandable that the improvement of cleanability of the toners is an area of focus of much research on the part of toner manufacturers as well as the hardware designers. Some research into the problem from the materials point of view promises solutions by surface and morphology modifications.

Double Layer / Core Shell

Zeon developed double layer / core shell type low temperature fixing chemically prepared toner and manufacture these toners for Brother and Oki. The fixing temperature of this toner is about 140ºC, and the toner has a wider fusing window than pulverized polyester based toner.

The toner has a mean particle size of 8.6 microns and has a suspension polymerized low melt core and a higher Tg shell. This results in a toner that utilizes low temperature fixing, about 20ºC lower than single structure toner. This enables a lower power consumption fuser could be utilized using 30% less power than the previous type.

The manufacturing method for the toner is that, firstly the core is polymerized by the usual method, similar to the Zeon "single structure" toners. This core contains not only the monomer for the core, but also the pigment, CCA and bulk additives such as waxes. The shell is polymerized in a second reaction. After completion of the polymerization, the subsequent steps in manufacture of washing, isolation, drying and blending of extra-particulate additives are then completed.

Zeon are developing their next generation microencapsulated toner, with 20 - 30ºC lower fusing temperature than the first generation product under the same conditions without severely losing anti-blocking features. They are also developing colored toners of similar technology and are working toward mono-dispersed particle size that they consider to be ideal.

The technique of making this double structure is an effective means to improving toner fixing performance. To create a clear boundary between shell and core is important. This may be achieved by manipulating the compatibility of the resin for the shell and resin for the core to be low. This control of compatibility is important. In use, the toner is subject to mechanical force from various rollers in the developing unit, and friction caused by the action of the doctor blade. If the boundary between shell and core is too distinctive (that is, resins have a too low compatibility) then the shell tends to be stripped from the core. Thus the boundary between the core and shell must be defined adequately enough so that the core and shell can function independently, but at the same time, with a level of adhesion, by virtue of the compatibility, to endure mechanical stresses in the print engine.

Zeon also completed formulation of suspension polymerized color toner in 2000. Scale up from the experimental level to mass production of 5-6 micron particle size toner has been under way, and they are working with hardware manufacturers who plan to use this toner on their hardware.

Canon

Canon uses this suspension polymerization for their colored laser printer toners. The toners are spheroid in shape, have a wax-rich core and the toner is designed to print matte color hard copy. Their toners can be fixed using oil-less fixing systems in their printers the release from the fuser rollers being achieved by the use of the wax-rich core. Originally Canon introduced their first generation of toners in the Canon LBP2140/HP4500. This engine used CPT Yellow, Magenta and Cyan color toners and a conventional black toner. They introduced the manufacture of black toner by suspension polymerization method in November 2000. First use of this black toner was in a 21-ppm dual component development engine.

Canon's chemically prepared toner production facilities are in the Toride factory (Toride-shi, Ibaraki-ken) and since the autumn of 2000, production started at Oita Canon Material (Kitsuki-shi, Oita-ken).

Canon S Toner Technology

The CPT materials were initially used in Canon Pixel L CP660 color printer. The

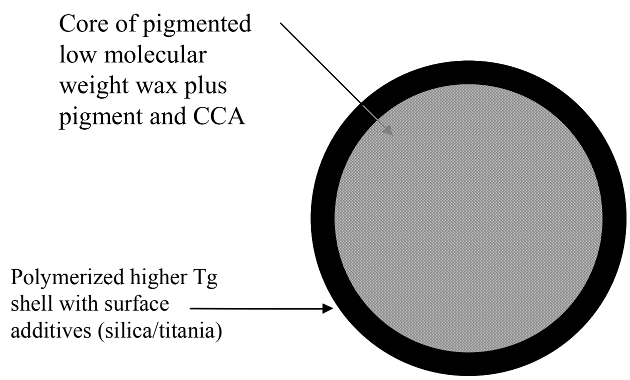
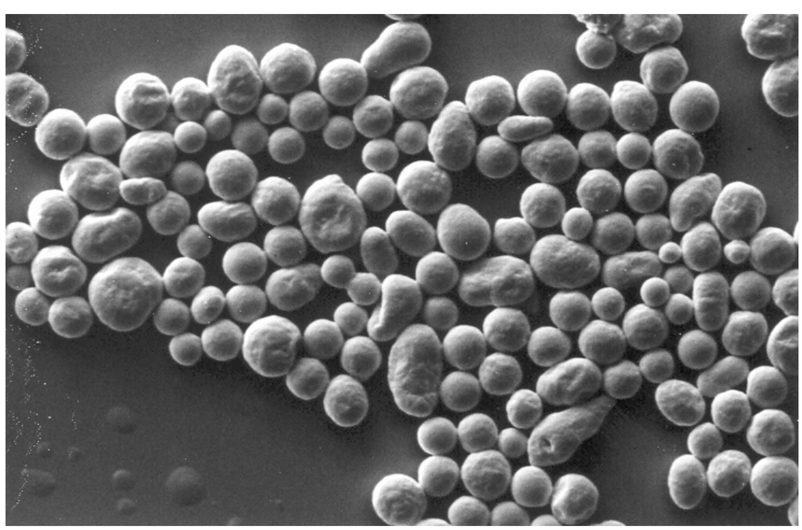


diagram below is a representation of the toner in cross section. The toners are microencapsulated 7.5 micron in mean particle size and have a protective shell of high Tg polymer with a quoted melt temperature of 74 °C. The core contained a very high concentration of low melt polyethylene wax that results in the compatibility of the toner with the oil-less fuser system. The fused toner produces matte prints with, what is considered by many to be, poor transparency. More recent generations of this toner are improved in this respect and now the transparency is more acceptable. The SEM below shows a close look at the toner.



Canon refers to this toner as their S toner. The SEM clearly shows the spheroid shape of their CPT. The properties of their toner impart better edge acuity, better, more even fill and less line spread.

From a technological standpoint, the CLJ 4500 pushed the envelope on several fronts. Its' use of chemically produced spherical toners was a first for Canon. Up to that point, Okidata had been the primary OEM using such chemically manufactured toners in its monochrome printers. Canon's elimination of the need for silicone oil wetting of the fuser, the first color laser engine developed that has eliminated all requirements for fuser oiling, meant a benefit cited by Canon in its press releases as a reduction in the glossiness of the output that rendered more accurate photographic reproductions.

The HP4500 also extended the partnering of HP and Canon from monochrome to color. Since November 1997, HP and Canon maintained exclusivity on all new Canon engines. This then extended to Canon's new color engines used in the Color LaserJet series. HP's superior brand identity built on its years of supplying monochrome Canon engines and its own color inkjet technology made the HP4500 the color laser printer with the greatest volume in all world markets. In 1999, the HP 4500 captured approximately 35% of 1999 color laser shipments in the U.S. Combined with the HP 8500, HP's market share was probably just over 40%. Since then, HP's color laser market share reduced slightly. Even though HP does not dominate the color market as they have the monochrome market, the HP 4500 became one of the most important new color laser engines.

One major reason for the success of Canon's toner in the marketplace has been their partnership with Hewlett Packard. The Hewlett-Packard Color LaserJet 4500 was a highly significant milestone for color laser printer market. Since the introduction of this model with its CPT cyan, magenta and yellow and black conventional toners, Canon have introduced the LBP2040, LBP2120, LBP2160 and IR3200 and HP have introduced the HP1500, HP2500, HP3500, HP3700, HP4550, HP4600, HP4650, HP5500, HP8500, HP8550.

Conclusion

Suspension polymerization provides and will continue to provide the toner manufacturers with a method of manufacture that enables the simple production of precisely controlled, narrower particle size distribution, super fine toner of higher flowability providing improvements in print image and print quality higher and with higher transfer efficiency and lower temperature fusing.