CHAPTER 1

INTRODUCTION

1.1 Introduction to electro photographic copying process

The invention of the electro photographic copying process must be viewed as one of the most significant inventions of the twentieth century. Laser printing technology evolved from Chester Charlson's electrophotographic inventions in 1938. It was further developed as a copying technology at Haloid Corporation which became Xerox Corporation in 1961. The first laser printer was developed by Gary Starkweather at Xerox PARC in 1971[1].

It is almost impossible for us to imagine how business was conducted before the existence of the ability to instantly generate, reproduce and transmit hard copy documents. For most of the copiers, laser printers and now facsimile machine, toner is an essential component.

Briefly, we will discuss how laser printers work and the role of toner. The primary principle at work in a laser printer is static electricity, the same energy that makes clothes in the dryer stick together or a lightning bolt travel from a thundercloud to the ground. Static electricity is the electrical charge built up on the surface of an insulated object. Since oppositely charged particles are attracted to each other, objects with opposite static electricity fields cling together. A laser printer uses this phenomenon as a sort of "temporary glue". The core component of this system is the photoreceptor, typically a revolving drum or cylinder. This drum assembly is made out of highly photoconductive material which can accept and retain electrostatic charges but will discharge by light photons [2-4].

The basic components in a laser printer are photoreceptor drum assembly, discharged lamp, developer roller, fuser, corono wire, hopper, and scanning unit. Figure 1.0 is the illustration of the basic components in a laser printer.

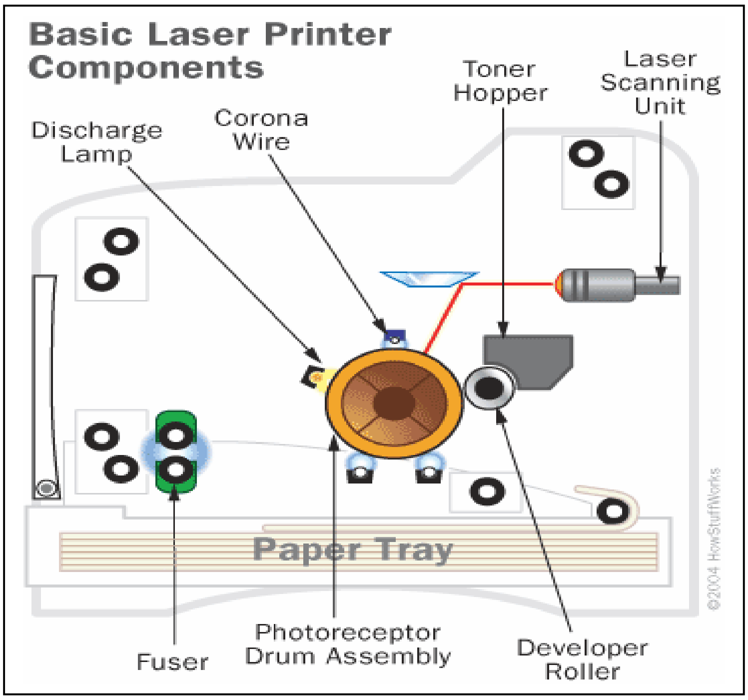

Figure 1.0: The basic components in a laser printer[75]

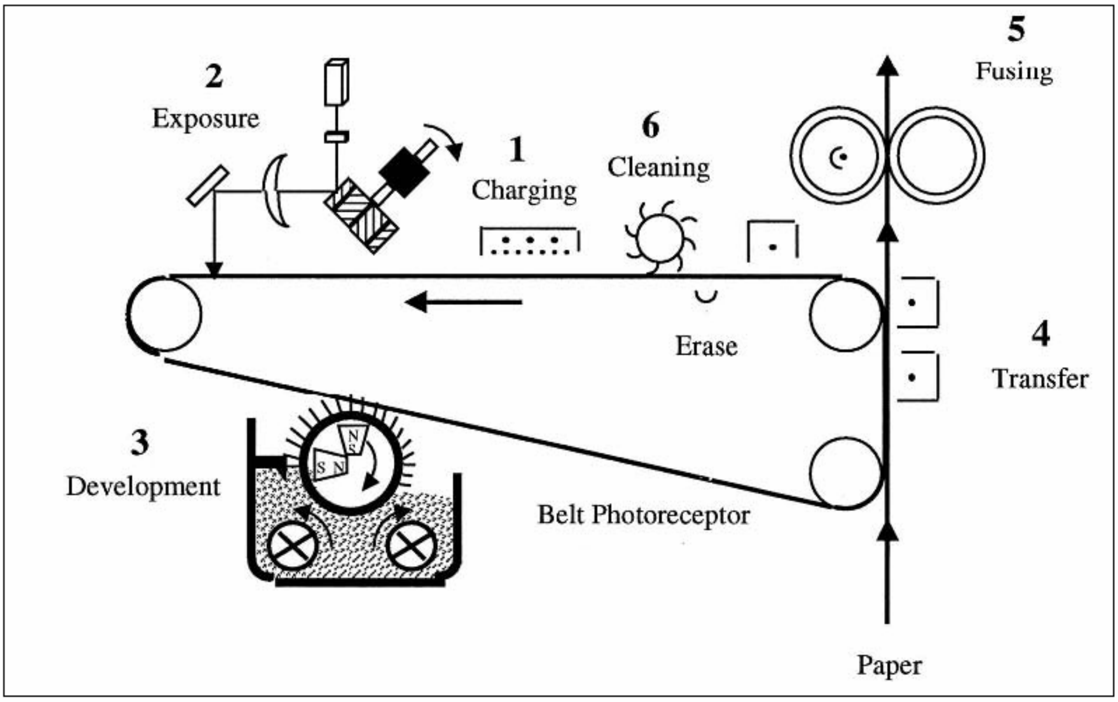

Figure 1.1: The basic steps in the xerographic process: (1) charging the photoreceptor, (2) exposing to form the latent image, (3) developing the latent image into a real image, (4) transferring the image to paper, (5) fusing the image to paper, and (6) cleaning residual toner from the photoconductor[75].

There are six steps to produce a hard copy output as shown in Figure 1.1. Initially a high voltage is impressed through the corona wire (some printers used the charged roller instead but the principle is similar) and charged air molecules or known as “ions” are created in the process. These ions are sprayed over the rotating photoreceptor drum, creating a uniformly charged surface. These charges may be negative or positive depending on the composition of the photoreceptor. As the drum revolves, the printer shines a tiny laser beam across the surface to discharge certain points. In this way, the laser "draws" the letters and images to be printed as a pattern of electrical charges which we refer as an electrostatic image or latent image [2-4].

In a laser printer, there are 2 concepts used in creating the images to be printed out on the paper by discharging the charges on the photoreceptor drum. When the tiny laser beam discharged the background charge as no toner will be deposited in this area is referred as “write white”. Alternatively, when the laser exposure is designed to discharge the image area is referred as “write black” as toner will be attracted to this discharged area. Figure 1.2 is the diagram showing the different of “write white” and “write black” concepts. “Write black” operation is that more commonly used because it is obviously faster to discharge 5% instead of 95% of the charges if only 5% image coverage on a document is needed to be printed out [2-4].

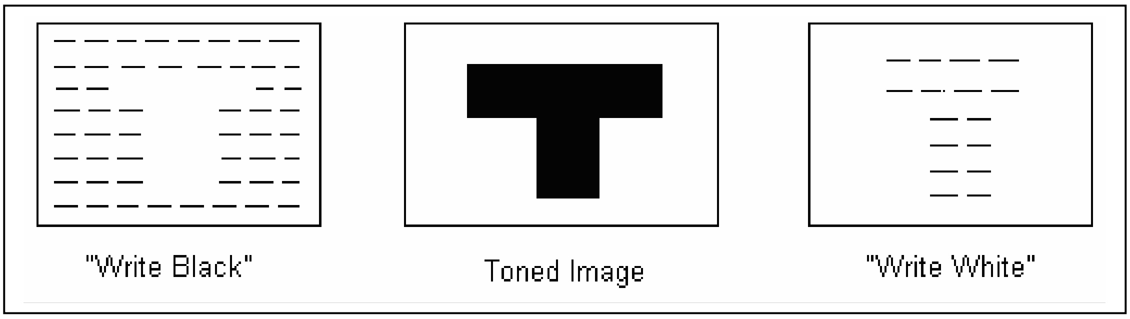

Figure 1.2: Laser printer exposure[2]

In a “write white” laser printer, the electrostatic “latent” image is toned with oppositely charged toner. On the other hand, in a “write black” laser printer, discharged image development is applied. In discharged area development, a bias voltage causes the image area to effectively have an opposite potential from the background areas. Thus a toner of the same polarity as the background is used. With the powder pattern affixed, the drum rolls over a sheet of paper, which is moving along a belt below. Before the paper rolls under the drum, it is given a negative charge by the transfer corona wire (or charged roller). This charge is stronger than the negative charge of the electrostatic image, so the paper can pull the toner powder away. Since it is moving at the same speed as the drum, the paper picks up the image pattern exactly. To keep the paper from clinging to the drum, it is discharged by the corona wire immediately after picking up the toner [2-4].

Finally, the printer passes the paper through the “fuser”, a pair of heated rollers. As the paper passes through these rollers, the loose toner powder melts, fusing with the fibers in the paper as shown in Figure 1.3. The fuser rolls the paper to the output tray with the required printed page. The fuser also heats up the paper itself, of course, which is why pages are always hot when they come out of a laser printer or photocopier. After depositing toner on the paper, the drum surface passes the discharge lamp. This bright light exposes the entire photoreceptor surface, erasing the previous electrical image. The drum surface then passes the charge corona wire, which reapplies the positive charge [2-4].

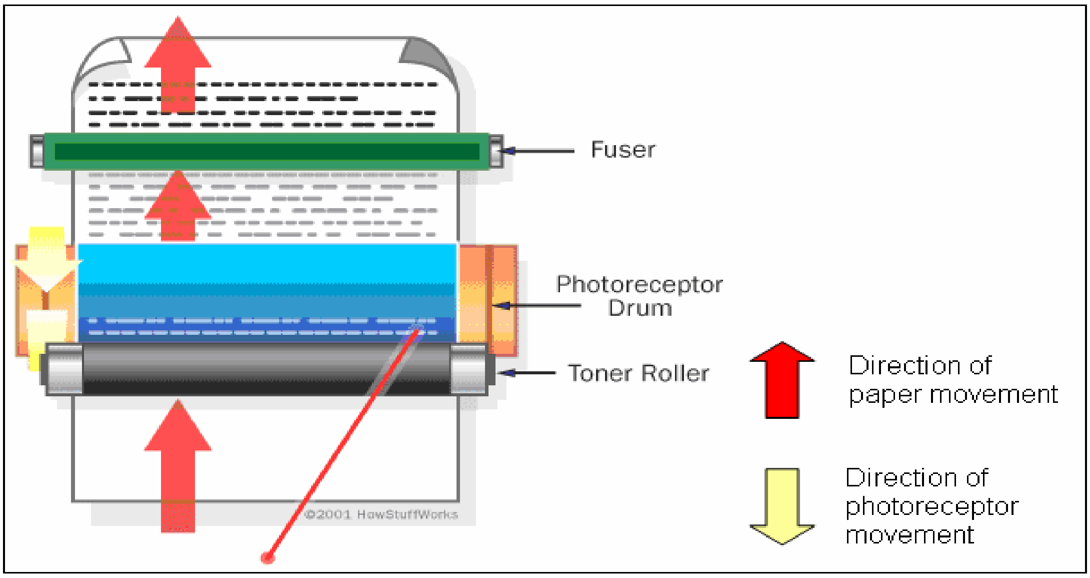

Figure 1.3: Schematic diagram of a paper passing through the fuser[2]

There will be typically 10 to 20% of the toner not transferred to paper. A brush, plastic scraper blade or occasionally the developer system itself will be used to remove this excess toner. This toner is then recycled back to the development chamber [2-4].

1.2 Introduction to toner

The most distinctive thing about a laser printer (or photocopier) is the toner. Toner is in powder form, it is a combination of plastic resins, pigments, waxes, flow agents, charge agents and magnetic compounds such as magnetic oxide (in the case of a magnetic toner). Toner is used in laser printers and photocopiers to form the text and images on the printed paper. In the earlier period, it is basically form from carbon powder. Then, to improve the quality of the printout, the carbon was blended with a polymer or resin with other additives like charge control agent, pigment and wax. Toner particles are readily melted by the heat of the fuser, causing them to bind to the paper. The specific resin used varies by manufacturers, most commonly a styrene–acrylate copolymer or a polyester resin. The toner formulations can vary from manufacturer to manufacturer and even from machine to machine since printers differ one from another by the temperature and construction of their heating devices as well as the number of other parameters [5,6].

The original particle size of pulverized toner averaged around 12 µm to produce a print resolution of 300 dpi. To improve image resolution, particle size was reduced eventually reaching about 8–10 µm for 600 dots per inch. Toner manufacturers maintain a quality control standard for particle size distribution in order to produce a powder suitable for use in their printers.

Toner has traditionally been made by compounding the ingredients and creating a slab which was broken or pelletized and then turned into a fine powder with a controlled particle size range by air jet milling. This process resulted in pulverized toner granules in varying sizes and shapes.

Recently, there are interests in research and development using a chemical process to produce toner particles which are known as the chemically produced toner (CPT) in order to produce better prints. This chemical process is able to produce more uniform size and shapes toner particles. The resulting smaller uniform shapes permit more accurate color reproduction and more efficient toner use [5,6].

1.3 Toner Compositions

Dry toners are formulated from as few as two to as many as six or more components. These components include resin, pigment, magnetic oxide, charge control agent (CCA) and additives. The actual toner composition for a machine will be dictated by a number of considerations. On the most basic level, the choice of components will be largely determined by the design parameters of the hardware system. Such factors as image quality, reliability and carrier life [2,5].

1.3.1 Resin

The main component in toner is the resin, which is also known as the binder. In most toner, the resin comprises up to 50% of the total toner composition. The role of the resin in toner is to bind the pigment to the paper or transparency material to form a permanent image. This is typically done by selecting a polymer that will melt at a reasonable temperature when heat is applied or one that can be forced into the paper fibers at high pressure without additional heat.

The resin also contributes to the other toner functions. It provides paper adhesion, assists charging, increases electrical resistivity that provides the mechanical integrity and allows cleaning of the photoreceptor. An “ideal” toner resin usually will have the ability to wet and disperse pigments, have physical properties that allow both functionality and compatibility with all machine sub-systems, be easily processable, non toxic and of reasonable cost. In fact frequently, a mixture of two or more polymers is required to achieve the desired results.

Several different types of resins (polymers) have found in frequent application in xerography depending on the fixing technique selected. The most commonly used resin in toner industry are polyesters and styrene-acrylate copolymer although others like acrylics, epoxy, polyamide, polyethylene, polystyrene, styrene-butadiene and modified polymers are used too [2,5].

By far the largest volume of toner resins has been various styrene-acrylate copolymers which are used in both negatively and positively charge toners. The desired physical properties are quite easily tailored via choice of monomers, polymerization technique and molecular weight distribution or polydispersity. Polyester posses many desirable properties which offer excellent pigment wetting, paper adhesion, high negative charging, easily controllable viscosity via composition or crosslinking and ease of toner processing particularly jet milling [2,5].

1.3.2 Pigment

Toners consist of four basic colours of cyan, magenta, yellow and black. Pigment can serve an important role to give out either strong or mild colour on the printed pictures. Colour pigment comprises about 5 to 15% of the total toner compositions. Carbon black is very commonly used compared to other black pigments. Carbon black can serve many functions in toner design. It has excellent heat and light stability and cheap in cost. Carbon black has a strong influence on the triboelectric charge. Oxidized blacks with acidic surfaces have long been used to increase negative charging but unfortunately, the best grades for this purpose are considerably more expensive. Most current toners include the additional of charge control agent (CCA) so there will be a tendency to use less structured and more easily dispersed carbon black [2].

1.3.3 Magnetic Oxide

About 50% of dry toner consists of magnetic iron oxide pigments. The principle of using magnetically attractable pigments is to control delivery of the toner on magnetic developer roll. This requires pigments with the appropriate magnetic strength.

The other function of the magnetic pigments is to contribute color as iron oxides are black or brown and frequently no other colorant is required. Typically, the magnetic pigments are Fe_3O_4 of cubical or spherical shape with particle size less than 0.5 μm. Frequently the magnetic pigments are surface treated with chemical compounds to improve their dispersion within the polymer, to adjust toner triboelectric properties, or most significantly to control humidity sensitivity of the toner [2].

1.3.4 Charge Control Agents (CCA)

Electrostatic charge of toner is a surface phenomenon. It is possible to control toner charge via toner composition, the carrier surface or a combination of both variables. In mid 70s, the industry began to see the introduction of Japanese toners which contained negative charge agents. These materials allowed toners to charge rapidly and maintain stable charge. The result was sharper, high density images, decreased in background and most importantly, the ability to design smaller developers units. Typical negative charge agents were metal dye complexes. The disadvantages of these materials are their high cost, high color tone and frequent concerns about toxicity. In general charge agent should pose the following characteristics: (1) rapid charging, (2) high charge magnitude, (3) charge stability, (4) thermal stability, (5) easily dispersible, (6) low electrical conductivity, (7) there is no interaction with photoreceptors, carrier coatings or fuser rolls, (8) non-migrating or blooming and (9) reasonable cost [2].

1.3.5 Additives

Many developer systems contain one or more additives. The majority of additives consist of fine particles physically blended with toner at 0.1 to 3% of the total toner compositions. These additives can be electrostatically attached to toners, physically attached via mechanical impact or heat softening, or occasionally just physically mixed but not attached. Some of the commonly used additives include silicas, waxes, metal stearates and conductive particles. These additives perform numerous functions including flow control, charge control, cleaning, fixing, offset, transfer, decrease humidity sensitivity, clean developer roller, increase carrier life and prevent photoconductor crystallization.

The choice of additive and method of addition are critical. Usually high speed mixers are necessary to achieve uniform additive blending. Such mixers may also generate sufficient heat to melt the toner which has formed large chips. A common problem is that one type of additive may have negative effects to that of another additive. For instance, many hydrophobic silicas will greatly increase toner flow characteristic but it will raise the triboelectric charge to unacceptable levels. This may necessitate addition of second additive to moderate the charge [2].

1.4 Toner Property Requirements

The principal requirement of any toner is to provide a desirable output image on some media, which is usually but not always paper. The acceptable image level is different for each observer. Some might want high optical density; others might want fine line resolution. Certain applications require a complete absence of background toner. However, design of the toner must also take into accounts its interactions with all machine components and development system such as photoreceptor drum, cleaning and fusing. In addition, the toner must be readily processable, stable to different environmental conditions, economical, odorless, and non-irritating and pose to no health risks.

The performance characteristics of this toner will be dictated by its physical, chemical and electrical properties. These properties are function of the formulation itself as well as the manufacturing processes[2]. Table 1.0 lists the most important of these properties in toner application.

Table 1.0: Toner Properties

Properties		
Physical	**Electrical**	**Thermal**
• Particle Size Distribution • Mechanical Strength • Powder Flow • Pigment Dispersion • Specific Gravity • Bulk Density • Shape	• Triboelectric Charge (Polarity, Rate, Charge Distribution, Stability) • Dielectrics (Dissipation Factor, Dielectric Constant Resistivity)	• Softening Point • Blocking Temperature • Melt Viscosity
Magnetic	**Colors**	
• Saturation • Remenance • Coercivity	• Cyan • Magenta • Yellow • Black	

1.5 Types of Toners

There are two types of toners available in the market at the moment, the conventional toner and the chemically produced toner (CPT). Both of these toners are very different either physically or chemically and are manufactured by different processes. The conventional toner is "top-down" in the sense that it pulverized a large mass of raw materials to make the toner particles whereas the CPT process is "bottom-up" since it grows the toner particles from small molecules by chemical synthesis and other physical aggregation as shown in Figure 1.4. The schematic schemes on how both processes work are shown in Figure 1.5. The brief explanation on these two processes will be discussed later.

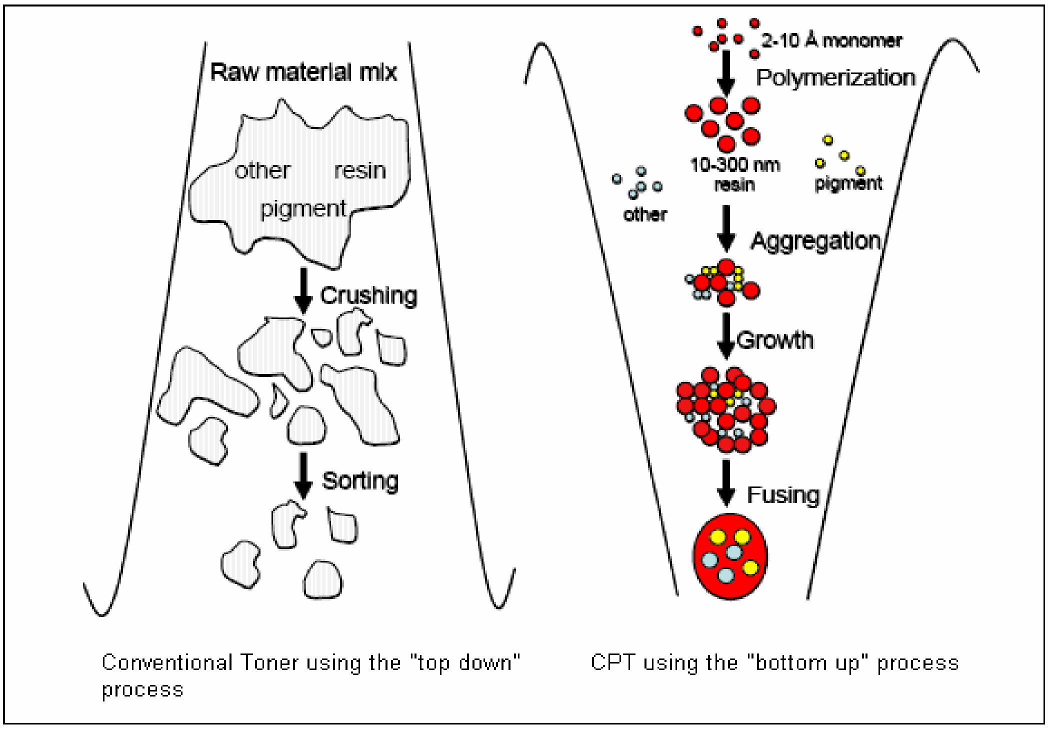

Figure 1.4: A comparison of the particle formation of conventional toner using "top up" process and CPT using "bottom up" process

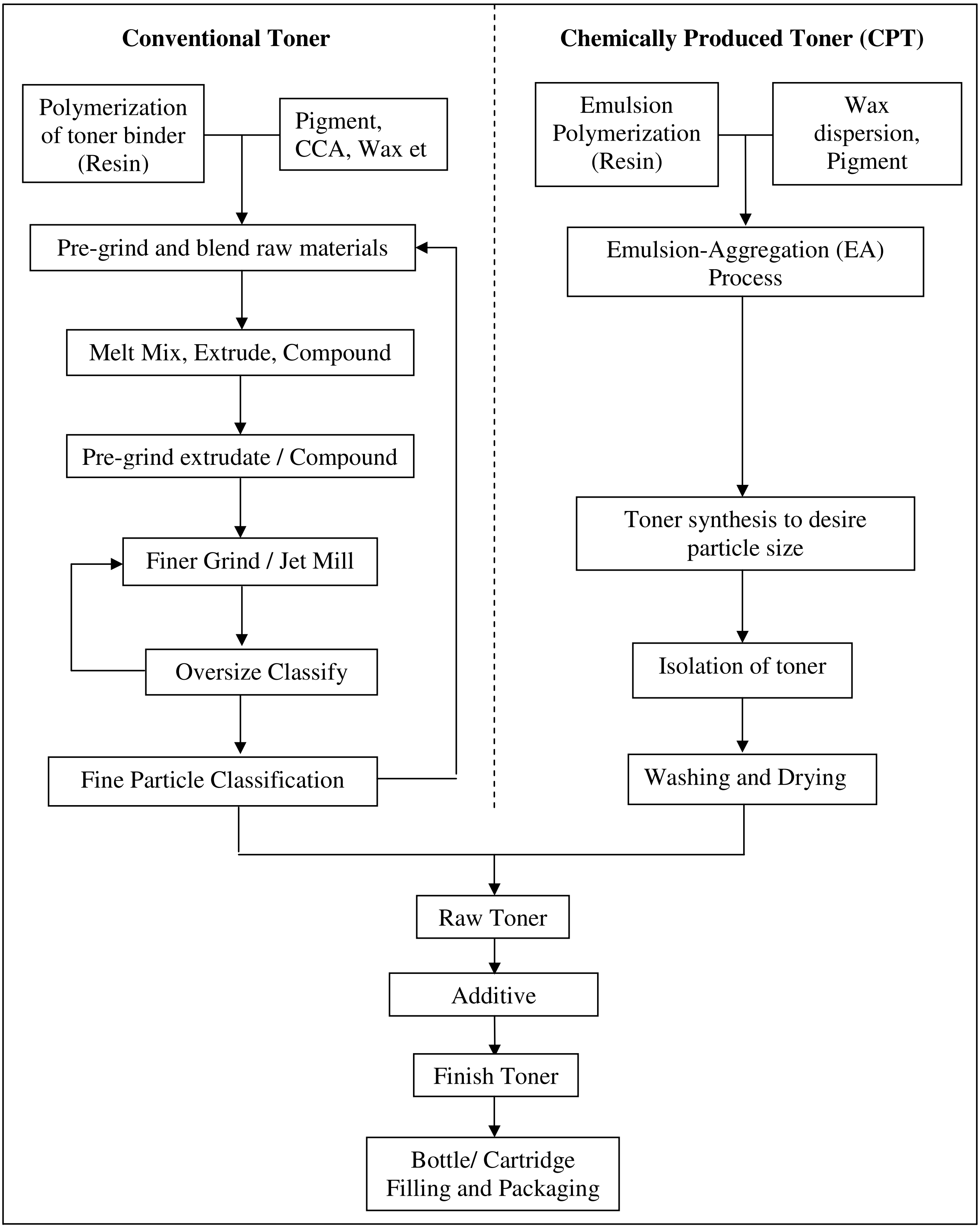

Figure 1.5: The schematic scheme on conventional toner and CPT manufacture[7]

1.5.1 Conventional toner

Conventional toner is also known as pulverized toner. The toner powders are prepared by a process consisting of melt compounding, milling, classification, and post-blending of surface additives. This process has been very versatile in producing different types of toners of different thermal and physical properties.

The components are mixed in the extruders or mixing devices. The temperature of the dry components is increased up to the melting point of the resin. At this temperature, the resin and other components are melted to form a paste. The homogenized mixture is poured on a flat plate to cool to form a hard piece. It is then crushed into pieces in the mill crusher. It is important to constantly control the milling time and temperature in the air crusher in order to maintain consistency of the product. The milled toners are then transferred to a classifier to sieve and separate particles of different sizes with the help of the high speed rotor. The product of correct particle size is withdrawn from the stream and the over size particles are put back into the mill crusher for further breakage. The classifying process is very important not only to sieve out the big particles but also to separate the undersize particles which can be loose resins, pigments or other additives which are not blended well together. These unblended materials can lead to undesired background or other printing defects. Conventional toner particles have uneven shape edges [5,7]. Figure 1.6 is the Scanning Electron Microscope (SEM) picture of conventional toner.

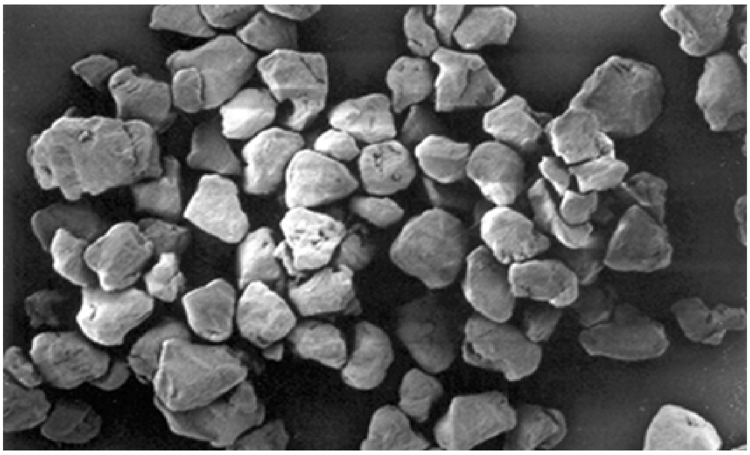

Figure 1.6: SEM picture of conventional toner[7]

1.5.2 Chemically produced toner (CPT)

Chemically produced toner (CPT) is toner made by chemical process. CPT is prepared by method which allows the control of particle size, particle size distribution, shape, morphology, structure and physical attributes related to toner functionality in printing system. CPTs have been marketed as providing a number of advantages over conventional toner. CPTs particles are smaller and more consistent, and capable of rendering better image quality.

In the past, conventional manufacturing processes have had an economic size limitation due to low manufacturing yields when pulverizing the toner to smaller particle sizes, whereas chemical toner production methods are able to produce small particles within a narrow distribution by either suspension polymerization or emulsion aggregation process.

The CPT is prepared chemically where toner is synthesized to desire size and shape through chemical process rather than being ground down like the traditional pulverized toner into irregular shape. The toner is washed and isolated out through filtration before drying in vacumn oven until the raw toner is ready for post-blending with other additives to produce finish toner[7-9]. Figure 1.7 is the Scanning Electron Microscope (SEM) picture of a CPT toner.

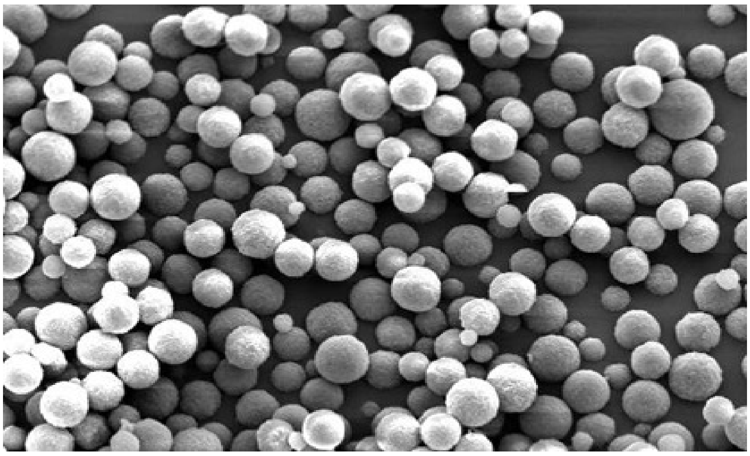

Figure 1.7: SEM picture of Chemical Produce Toner (CPT)[7]

The chemically produced toner can appear in the shapes of sphere, potato, and popcorn. The different shapes of toner can have different efficiency in electrographic technology. Figure 1.8 showed the diagram of how these shapes look like and how it influences the efficiency in electrographic industry.

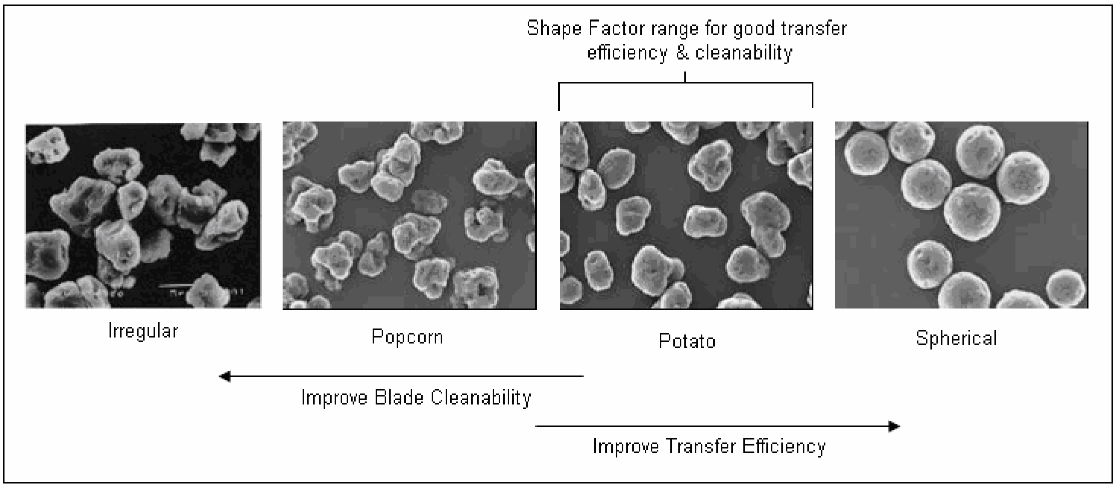

Figure 1.8: The chemically produced toner shapes and the effect on printing efficiency[7]

1.5.3 The advantages of CPT over conventional toner

Investment in chemically produced toner manufacturing goes up rather slowly because of the high production costs that involved. Besides, the development of new toner technologies also needs new equipments that are very expensive. However, still many large corporations like Mitsubishi Chemical, Konica Minolta, Tomoegawa and many more produce CPT because of the advantages of such toners.

The most significant advantage of CPT over pulverized toner on printing is the small mean particle size of toner. The smaller the mean particle size toner used to form an image, the lower the toner pile height is in the image areas which mean the toner transferred mass per unit area is lower. In short, CPT coated on paper surface with thinner layers of toner which directly diminished the consumption of toner on a unit surface like shown in Figure 1.9.

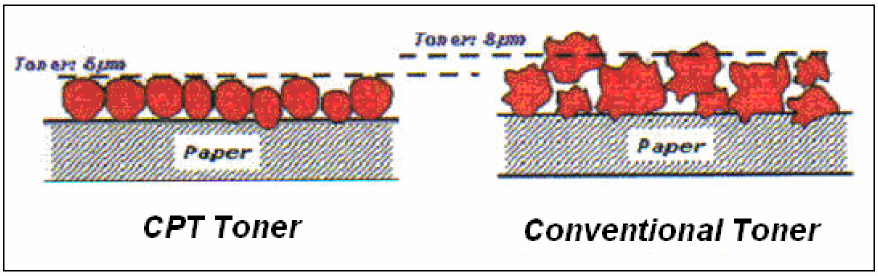

Figure 1.9: Thin layer of CPT and conventional toner on a paper surface[5]

The thinner of toner layered also means that the toner is more nearly conforms to the paper surface which means reduce in differential gloss which is the difference in gloss level between the toner image and the image background paper surface. Perfection would be “conformal gloss” such that there is no difference between the gloss of the image and the gloss of the paper. Small particle size toner also results in better lines and edges. Page curl is a result of the differential absorption and release of moisture barrier in regions and on one side of the printed page which causes curl and cockling. Thinner layers of toner can reduce this phenomenon [7-10].

CPT allows sticking toner to printing supports with higher precision. This makes printing of half-tone color transition and text with clearer contours as well as contributes to increasing the degree of discernment of small fragments and exact transfer of photo and graphic images [7-10].

Lower melting temperature of CPT owing to smaller spherical particles has benefits in easier fusing and fixing. Lower energy is required in fixing and indirectly reduces the energy cost with lower power requirements there is a potential to reduce hardware cost by reducing fuser cost. As a result, CPT increases the quality of prints at higher printing speeds.

CPT penetrates with deeper fixing onto paper which then increase the durability of prints and thus increase the resistance to light. Conventional toner may result in undesired background because of small particles obstructing the cartridge which rarely happen in CPT [7-10].

The usage of CPT will increase the durability of the organic photo conductor (OPC) drum because of its spherical or almost spherical shapes whereas, the sharp edges of conventional toners always scratch on the OPC drum which reduce the durability. Lastly, CPT is more environmentally friendly as scientifically proven that CPT manufacturing released carbon dioxide, nitric oxide, and sulfur oxide by 30-40% less as compared to conventional toner manufacturing [7-10].

1.6 Chemically Produced Toner (CPT) Manufacturing Methods

There are various methods used in the market to manufacture CPT. Different manufacturer will have their own methods to produce their own CPT which is compatible with their printers. The common methods used include suspension polymerization [11-13], condensation polymerization, dispersion polymerization, emulsion-aggregation polymerization [17-19], microencapsulation [14-16], and chemical milling [20] although dispersion and condensation polymerization are less popular used.

1.6.1 Suspension Polymerization

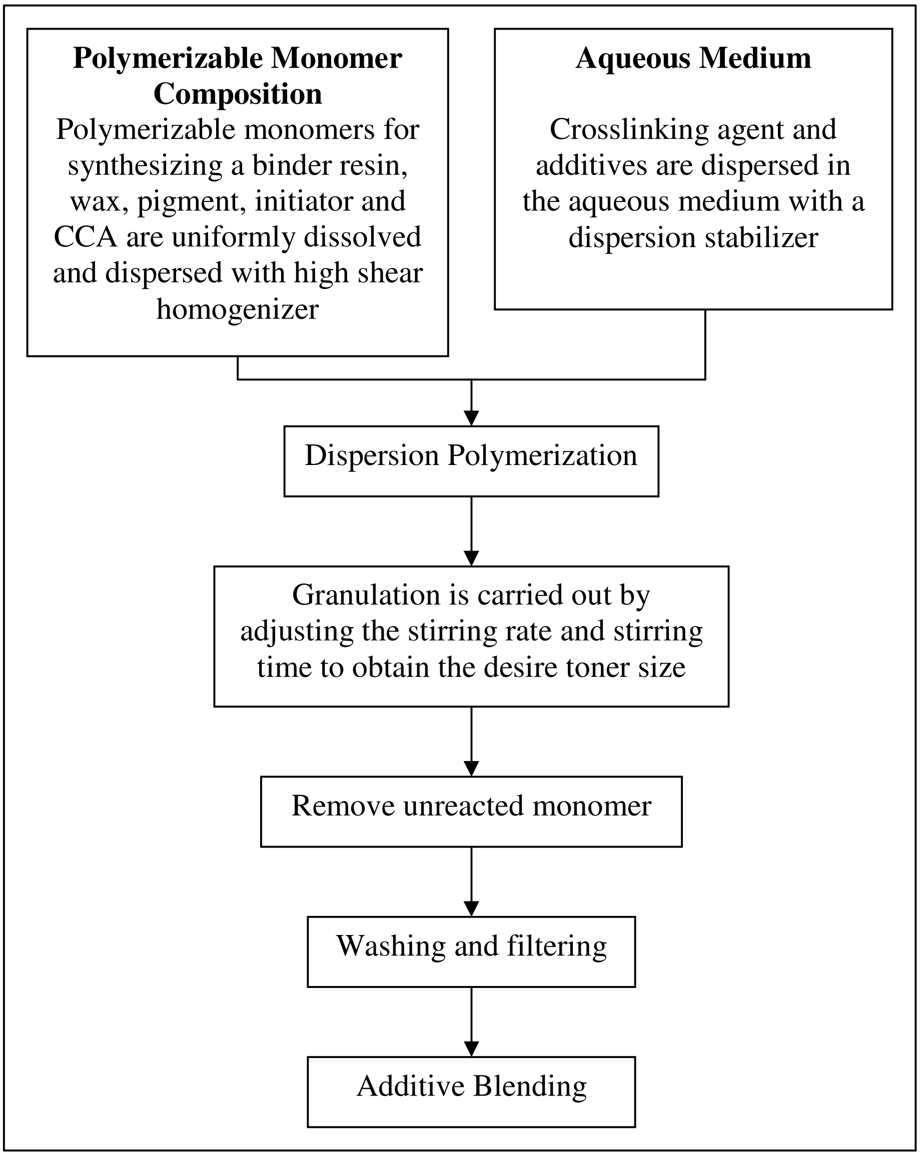

Figure 1.10: Flow chart of suspension polymerization[11]

Suspension polymerization is similar to bulk polymerization, and it could be considered "bulk polymerization within a droplet". For suspension polymerization, there are two separate phases which are the water (or aqueous) and organic phase. The initiator used is soluble in organic phase. Suspension polymerization is a process in which monomers are dispersed by mechanical agitation in a liquid phase where these monomer droplets are polymerized in shapes of the droplets. The monomer is mechanically dispersed in the water phase which serves as the heat transfer medium. Since this is a continuous phase, viscosity changes very little as the monomer converts to polymer [24].

The usage of small part of dispersion stabilizer with either just phosphate metal such as magnesium phosphate or it can be used with the combination with organic compound such as poly(vinyl alcohol) are required to prevent agglomeration. The droplets must be kept apart and hence there must be consistent, efficient and controlled agitation. In the system, the monomer must be either insoluble or slightly soluble in water so that when it polymerizes, it becomes insoluble in water [21].

Figure 1.10 shows a flow chart on the suspension process. The monomer mixture is introduced into the high shear to homogenize. After the dispersion step, the pre-homogenize dispersion is collected and mixed with wax, pigment, charge control agent and resin at 60°C, followed by the addition of initiator, hence a polymerizable monomer composition is prepared. Meanwhile, a slightly water-soluble dispersion stabilizer or known as the suspending agent is prepared and transferred into a four-necked vessel with high-speed stirrer and heated to 60°C. At this temperature, the above prepared polymerizable monomer composition is put into aqueous dispersion medium with continuous stirring. At this stage, the granulation steps will take place by adjusting the stirring rate and time as well as the reaction temperature to obtain the desire particle size toner particles.

After the polymerization is completed, the toner slurry is isolated, washed and dried before additive blending.

There above explanation is just an example on suspension polymerization as there are many other conditions and formula to do suspension polymerization toner in the market [11, 22-23].

1.6.2 Dispersion Polymerization

Dispersion polymerization has some similarity to suspension polymerization but is less useful in toner application because of the difficulties to incorporate bulk additives like waxes and charge control agents.

1.6.3 Chemical Milling Process (CM)

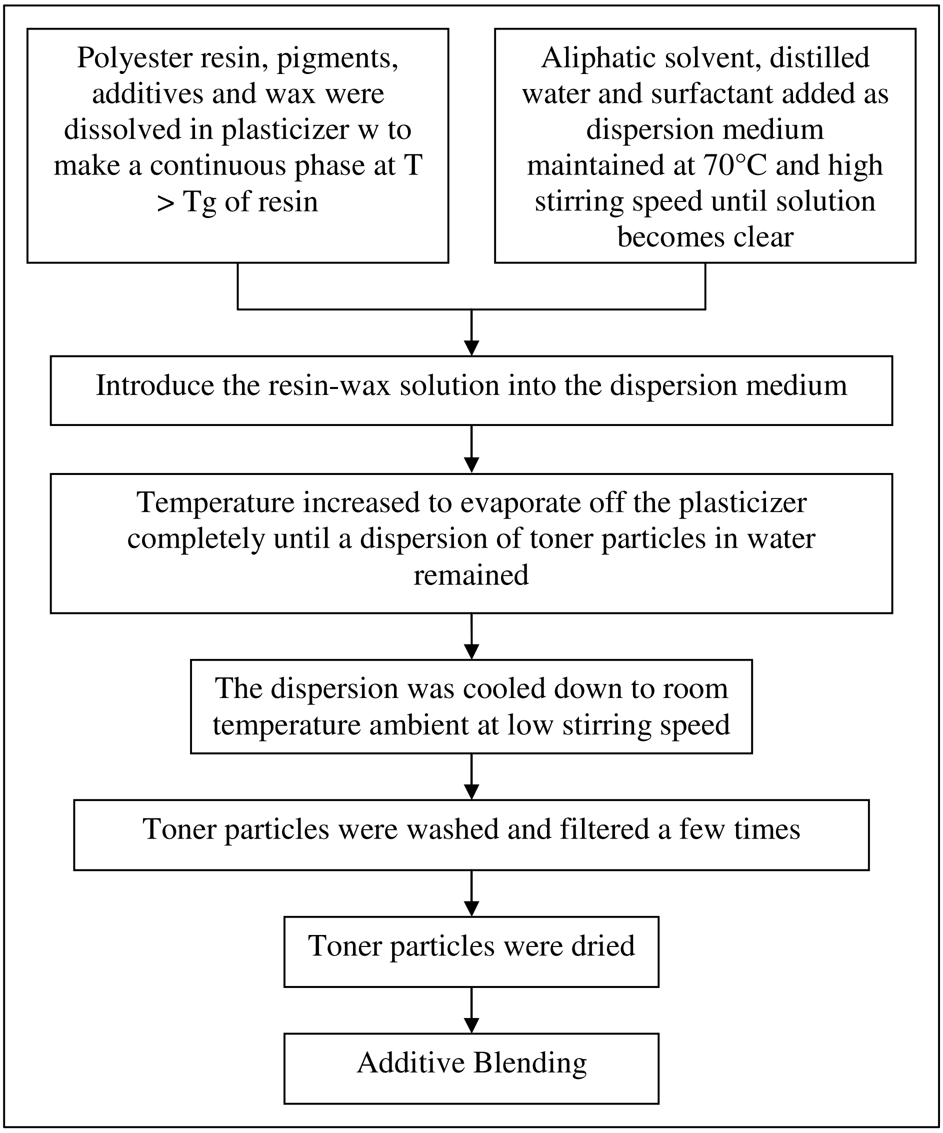

Figure 1.11: Flow chart of chemically milling (CM) process[20]

There is no polymerization steps involved in this technology. The technique is capable of using commercially available binder resins though the preferred type would be polyester. One of the main advantages of this process is capability to control surface morphology of the spheroidal particles besides having narrow particle size distribution. Production equipment for this technology is relatively simple and low in capital cost.

Figure 1.11 shows a flow chart on the chemically milling (CM) process. The polyester resin is added into a vaporized plasticizer such as ethyl acetate. The mixture is heated until the polyester resin is completely in molten stage where the mixture becomes homogenized and the wax, pigments and additives are added at this stage. Meanwhile, a reflux condensation reactor is prepared where aliphatic solvent, distilled water and surfactant are added to form dispersion medium.

The mixture is then added into the dispersing medium with continuous high shear speed stirring. Finally, the temperature is increased to evaporate off the plasticizer completely until a dispersion of toner particle in water remained. The crude toner particles are filtered and washed for few times before drying. The process is completed with additive blending [20, 24-25].

There above explanation is just an example of chemically milling process as there are more than one conditions and formula to do chemically milled toner in the market.

1.6.4 Microencapsulated Milling Process

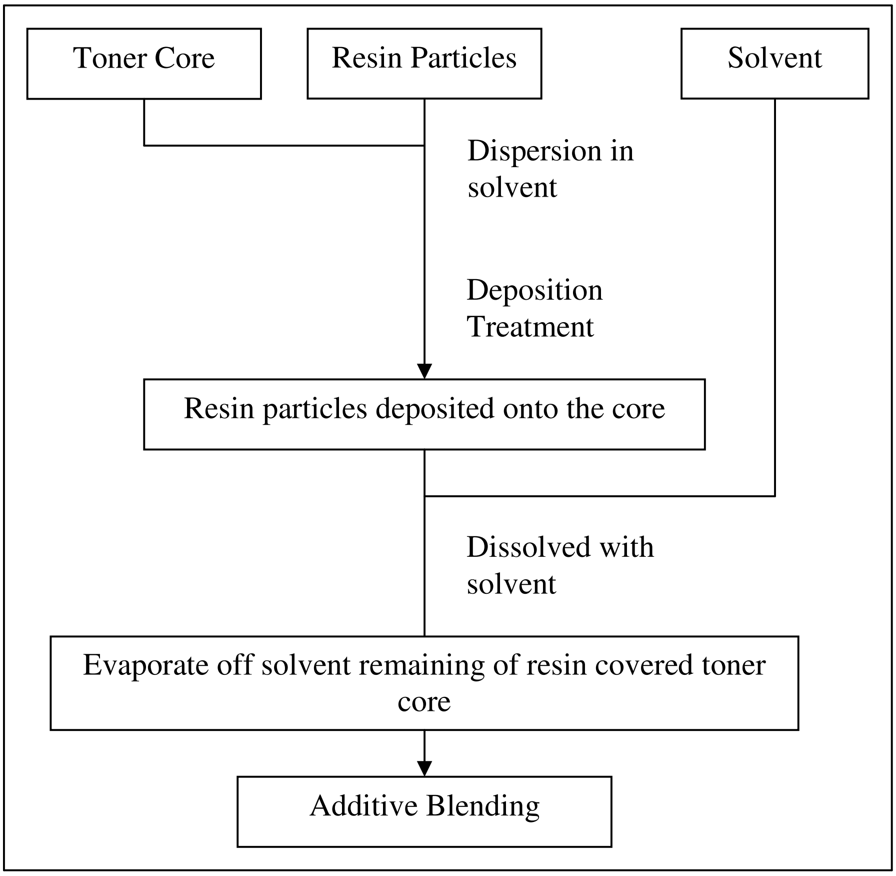

Figure 1.12: Flow chart of micro encapsulated milling process[26]

In the microencapsulated process, the toner particles produced have a core-shell structure. The properties of the toner particles are derived from both shell and the core. The properties derived from the shell contribute to the mechanical strength and thermal stability to prevent blocking during storage period especially under high temperature. The morphology and compositions of the shell will affect the flowability and triboelectric properties.

The properties core will affect the fusing and fixing properties determined by the compositional melt rheologies that can be adjusted by chemical composition and molecular weight. The core of the microencapsulated toner usually contains pigments. Microencapsulated process can be done in various coats on various cores at any desired with uniformly controlled coat thickness.

Figure 1.12 shows the microencapsulated milling process. The resin particles are deposited uniformly onto the surface of the microencapsulate cores. There are no limitation imposed on techniques to achieve depositions of the resin particles at this step, if to enable the resin particles to be deposited uniformly onto the surfaces of the microencapsulate cores and make their depositions and the number of resin-particle layers formed controllable by doing it with a gas stream or dispersed in liquid.

The resin-core particles are brought into contact with solvent where the resin can dissolve which means after the solvent evaporated off after contacting the resin-core particles will leave a uniform resin coat on the surface of the toner core. The solvent used can be chosen depending on the resin used, the solubility of the resin, and the manner and time of contact. However, the process of spraying the solvent onto the resin-core particles carried with a gas stream is preferred than rapidly dissolving resin-core particles with solvent because the time of contact of the resin-core particle with the solvent can be reduced to the maximum.

The solvent is evaporated off to leave uniform resin coats on the cores surfaces. The toner particles have to remain in the monodisperse state; carried out in gas stream or heated gas if required in order to prevent coagulation of the particles [26-27].

1.6.5 Emulsion-Aggregation (EA) Polymerization

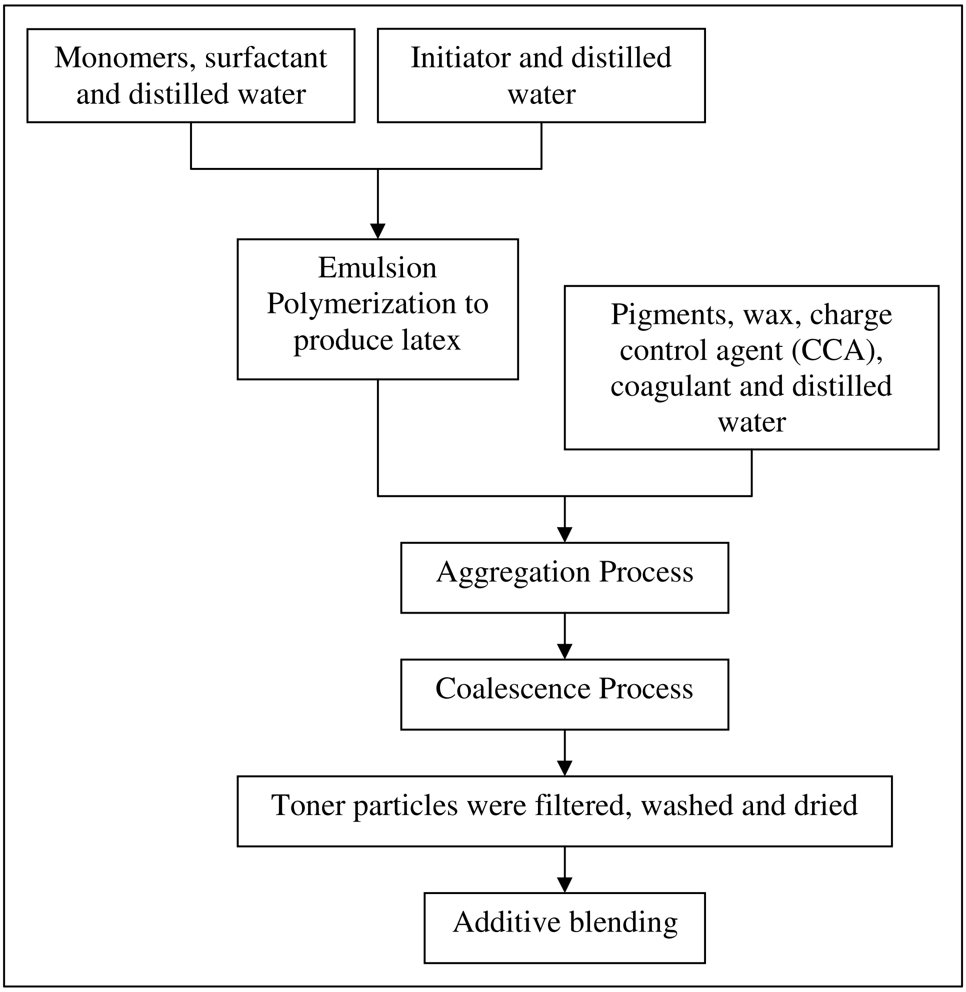

Figure 1.13: Flow chart of emulsion-aggregation process[7]

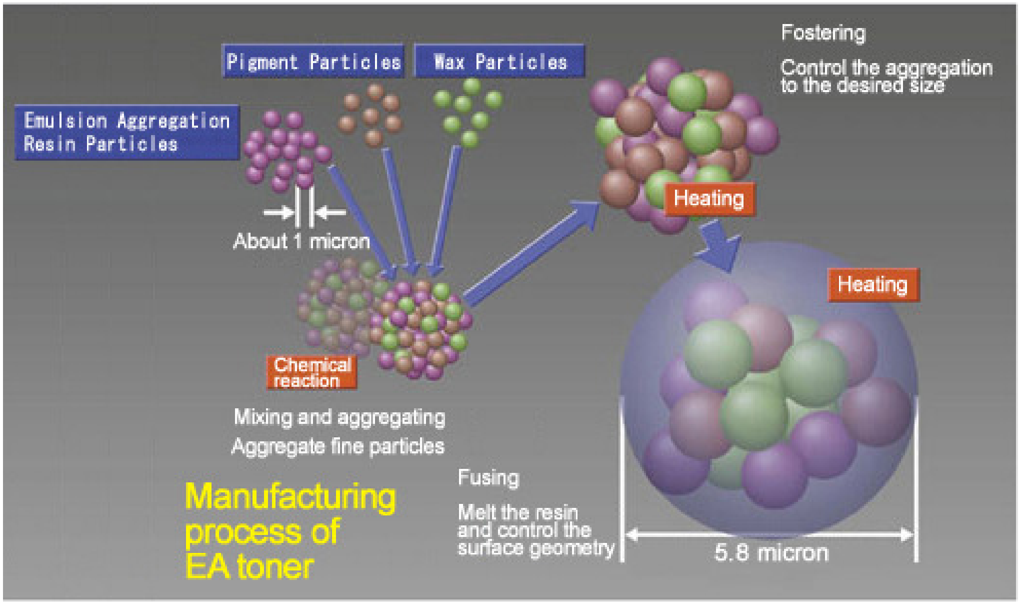

Figure 1.14: Manufacturing process of emulsion-aggregation process[7]

An emulsion is a system with two liquid phases; dispersed phase and continuous phase. The two liquids are usually mutually immiscible but there is a time where there is partial solubility. When the equilibrium solution becoming the continuous phase, that is when an emulsion is formed. There are two classes of emulsion which are oil in water (O/W) and water in oil (W/O). In order for emulsion to stay stable and not separate into two layers, a suitable stabilizer or emulsifier must be present.

In conventional emulsion polymerization, an aqueous dispersion of monomer(s) is polymerized by free-radical initiator to produce a stable emulsion of polymer particles of 0.1-1µm in diameter. A typical polymerization recipe comprises the aqueous medium (water), monomer(s), a water soluble initiator and emulsifier(s). The emulsifier serves as a stabilizer in the aqueous medium in formation of micelles (5-10 nm in diameter). A very small part of the monomer is usually present in the aqueous medium (water phase), some monomers migrates into the micelles but initially most monomers stay in the monomer droplets. The polymerization occurs either in the interior of the micelles known as the micellar nucleation or in the continuous phase known as homogenous nucleation. The disadvantage of emulsion polymerization is that the emulsifier used is a kind of soap and it contaminates the polymer. However, the advantage of the process is that there is better heat control because water is the polymerization medium. The size of emulsion polymerized particles is usually in the 0.05 to 5 µm diameter range [28].

In toner application, the other necessary components of toner such as pigment, charge control agent, wax cannot internalize into the polymer particles because such materials cannot diffuse into the micelle. If toner particle formation is attempted by direct combination of these components at the emulsion polymerization stage, they will reside on the polymer particle surface where they will affect the dispersion stability of the emulsion and cause coagulation.

Figure 1.13 shows a flow chart on the emulsion-aggregation process and Figure 1.14 shows a diagram of manufacturing of CPT using EA process. The most essential material for the emulsion-aggregation polymerization is latex. The aggregated toner particles are made from mixture of different latexes with differ in molecular weight and T_g. The latexes are produced by reacting monomers of desired ratio, emulsifier, initiator, distilled water and chain transfer agent with the semi-continuous method. The prepared latex and other additives like wax, pigment dispersion and coagulant are premixed and homogenized well in an aqueous medium. The mixture is then transferred to reactor flask and allowed it to heat to the temperature near the latex T_g which can be lower or higher; usually in the range of 53 to 57°C and maintained for 2 to 4 hours. The mixture is adjusted to pH 6 to inhibit the aggregation of the particles and the temperature is risen a lot higher than the T_g of the latex; usually in the range of 90 to 98°C. The mixture is adjusted to pH 8 to allow for the coalescences process for another 2 to 3 hours. The mixture is allowed to cool to room temperature upon completion and the slurry is isolated out, filtered, washed and dried. The dry raw toner needs to go through post-blending with the addition of other additives to form finished toner [29-35].

1.7 The Chemically Prepared Toner (CPT) Market

The worldwide toner production volume in 2001 reached 150,000 tonnes, 48% by Japanese manufacturer and 52% of the total made by non-Japanese manufacturer[7]. It is estimated that the worldwide toner production volume in 2007 will be more than 195,000 tonnes, about 30% increased over 2001. From 2002 onwards, there will be a trend in the Original Equipment Manufacturer (OEM) toner manufacturer selling OEM toner to other OEMs. In 1999, the proportion of all toners manufactured by chemically prepared toner technologies is only 1.6% of the world production and it is expected to rise more than 6.7% of world production by 2007. This growth, despite relatively small in volumes but it is significant. Figure 1.15 shows the volume of production by the major manufacturer from 1999 to 2006. The total amounts of CPT (black and color) toner manufactured by big corporation from 1999 to 2006 are shown in Table 1.2 [7].

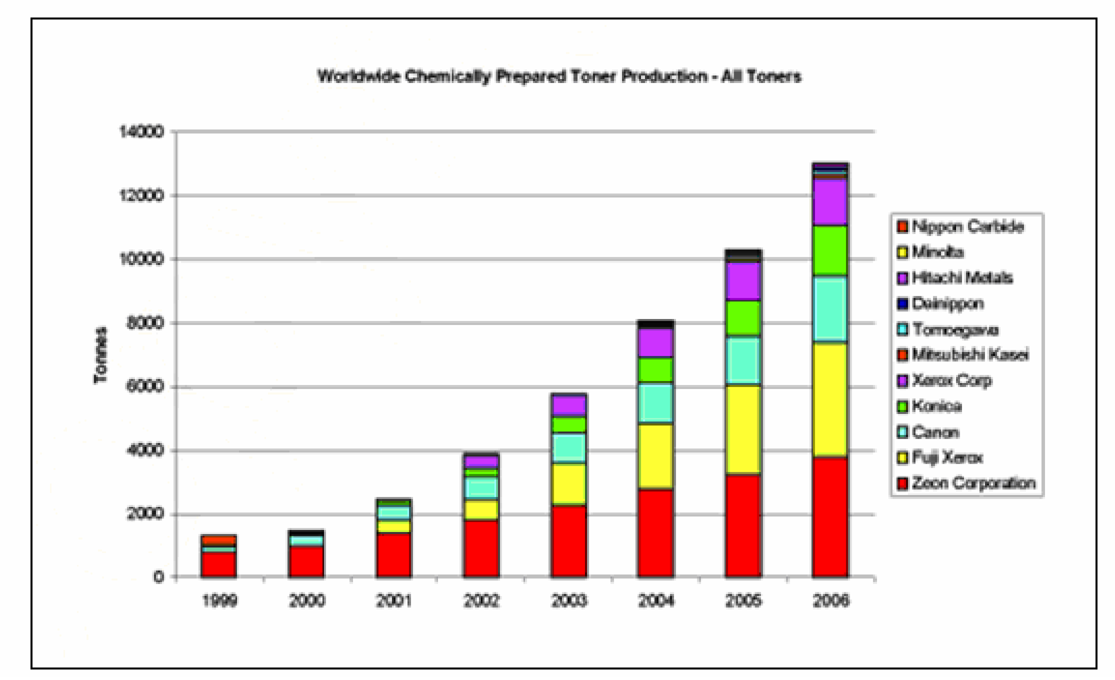

Figure 1.15: The volume of production by the major manufacturer from 1999 to 2006[7].

Table 1.1: The worldwide production of CPT[7]

	Chemically Produced Toner – Worldwide Production (tonnes)							
	1999	**2000**	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**
Zeon Corporation	800	1000	1400	1800	2300	2800	3250	3800
Fuji Xerox	0	0	400	650	1300	2050	2800	3600
Canon	180	340	490	720	970	1280	1550	2075
Konica	0	50	130	260	520	800	1100	1600
Xerox Corp	0	0	0	425	650	930	1225	1475
Mitsubishi Kasei	0	0	0	0	0	50	100	125
Tomoegawa	0	0	0	0	0	50	100	125
Dainippon	0	0	0	0	0	50	75	100
Hitachi Metals	0	0	0	0	0	50	70	100
Minolta	25	30	30	30	30	30	30	25
Avercia	0	0	0	0	0	0	0	0
Nippon Carbide	320	60	0	0	0	0	0	0
Total	1325	1480	2450	3885	5770	8090	10300	13025

Many big corporations are spending millions of dollars in research and development on chemically produced toner (CPT) because they see the potential on it. Table 1.3 below shows a listing of all the companies known to be involved in CPT production or research & development (R&D). This list is most likely not complete but includes the major known contributors [7].

Table 1.2: Listing of all the companies known to be involved in CPT production or research & development (R&D)[7].

Company	Produces CPT	R&D into CPT
3M		√
Avecia		√
Canon	√	√
Dainippon Ink & Chemical		√
Eastman Kodak / Nexpress		√
FDK		√
Fuji Photo		√
Fuji Xerox		√
Fujikura Kasei	√	√
Fujitsu		√
Hitachi Chemical		√
Hitachi Metal		√
Huber Munchen		√
Kao		√
Konica / Minolta		√
Kyocera Mita	√	√
Mitsubishi Chemical		√
Mitsubishi Paper		√
Nippon Paint		√
Nippon Shokubai	√	√
Nippon Zeon	√	√
Ricoh		√
Samsung		√
Seiko Epson		√
Tomoegawa		√
Toshiba		√
Toyo		√
Xerox Corporation		√

1.8 Scopes of Study

In this project, the main studies are the synthesis of styrene-acrylate copolymer using the semi-continuous emulsion polymerization to produce styrene-acrylate copolymer latexes. The styrene-acrylate copolymers were characterized to obtain the suitable properties in latexes. The copolymer latexes with suitable properties were proceeded to be used in the emulsion-aggregation process to produce raw toners with appropriate characterizations. The raw toner then undergoes additive blending to produce finished toner before using it to perform test print on the printer.

The first chapter contains brief introduction of electrographic technology, the introduction on toners, the two types on toners in the market which are the conventional and chemically produced toner, the toner manufacturing technologies and the toner industry market in worldwide. Chapter 2 describes the synthesis of styrene-acrylate copolymer latexes which includes the experimental works in the preparation and the characterization on these copolymers. By using the latexes produced, the emulsion-aggregation process was carried out to produce the raw toner by incorporating the copolymer latexes with pigments, waxes, coagulants and other additives and characterizations done on this raw toner were also described in Chapter 2. The additive blending of the raw toner to finished toner before proceeding to test print on the printer was also described in Chapter 2. Chapter 3 contains results relevant to the experimental and characterization works done in Chapter 2. Chapter 4 includes a summary and some suggestions for future works.