CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Theoretical background

2.1.1 History of Electrophotography

The active history of electrophotography began with the inventions of Chester Carlson in 1938. He used sulfur as a photoactive material to make images. In 1959, Haloid Corporation (now in the name of Xerox) introduced a 914 automatic copier, which used amorphous selenium as a photoreceptor, and this machine used the first commercial negative dry toner, styrene-methacrylate copolymers. During the 1970s, IBM and Kodak developed and introduced copiers based on organic photoactive materials and positive charging toners. During the 1980s, Japanese manufacturers, such as Canon and Minolta, produced low speed copiers based on selenium and cadmium sulfide photoreceptors using negative toners. They also introduced dry toner copiers using a single-component developing mechanism, eliminating the use of carrier beads. Since the 1980s, many combinations of single- and two-component developments, and positive and negative toners have been used in the industry [3].

2.1.2 The Electrophotographic Process

The electrophotographic process is based on six basic steps in reproducing a document: charging, exposure, development, transfer, fusing and cleaning as shown in Figure 2-1. First (the charging step), the photoreceptor is covered with ions through the use of a wire or grid biased to high voltage. Second, (the exposure step), an optical system forms an image of the document on the photoreceptor. This step forms a latent electrostatic image on the photoreceptor drum. Third (the development step), a toner of the opposite sign from the latent image is typically brought into contact with this image. Next (the transfer step), the backside of the paper which is brought onto the photoreceptor, is charged with ions opposite in polarity from the toner. This step transfers the image to the paper. Then (the fuser step), the toner is melted onto the surface of the paper. Finally (the cleaning step), the small amount of toner remaining on the photoreceptor after transfer is removed by an electrostatic brush [3].

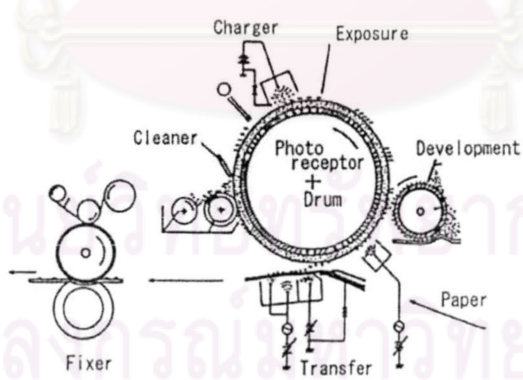

Figure 2-1 The electrophotographic process

2.1.3 Toner components

Dry electrophotographic toner consists mainly of a colorant in a binder resin. Besides these essential ingredients, a particular toner design may contain charge control additives, surface additives, magnetic additives and other additives such as wax [4].

2.1.3.1 Resin

The role of resin in a toner is to bind the pigment to the paper or transparent material to form a permanent image. The selection of the polymer depends on the fusing or melting properties and the fusing method, which can be subdivided as follows.

a) Cold pressure method

The materials for this method are typically lower molecular weight polypropylenes, polyethylenes, ethylene-vinyl acetate copolymers, and a mixture of these materials. These cold pressure fixing materials have the advantage of requiring low power in operation and no standby power.

b) Continuous radiant source

A quartz lamp or heated coil is commonly used to melt the toner into the paper fibers. The viscosity of the toner usually is of quite low melt in flowing into the paper. The polymers such as polyesters and epoxies, which have a molecular weight ranging from 5000 to 50000 and glass transition temperature from 50 to 60°C, are often used.

c) Flash fusing

The toner is melted into the paper by a very short, high intensity flash of light lasting less than 5 ms. Styrene copolymers, epoxies, and polycarbonates have used this fusing technique for fixation of toner images.

d) Roll fuser

The paper with the un-fused toner passes through a nip formed by a heated roll and a backup roll forced against the heated roll at fairly high pressures. The polymers used are styrene copolymers such as styrene acrylates, methacrylates and butadienes, which have molecular weights ranging 30000 to 100000 and glass transition temperatures ranging from 50 to 65°C.

2.1.3.2 Colorants

The most common colorant for electrophotographic toner is carbon black. Important properties of carbon blacks for applications are their dispersibility in the polymer resin and their tendency to charge either positively or negatively. Carbon black is usually used in toners at 5 to 15% loading. Besides carbon black, there are other materials that can be used to make black toners, for instance, magnetite is used to control magnetic properties of toner, and nigrosine is used as charge control agent as well as black pigment. For full color electrophotography, the organic pigments are usually used, such as, copper phthalocyanines are used for cyans and blues, azo pigments for yellows, and quinacridones or rhodamines for magentas and reds.

2.1.3.3 Charge control additives

Charge control additives, CCA, are added to the toner when the pigment blended into the polymer does not give an adequate charge level or rate of charging. For positive images, the quaternary ammonium salts are usually used in color toners because they are colorless. The other is nigrosine, which is black and used in black toners. For negative applications, acidified carbon blacks, fumed silicas and metal complexes are used.

2.1.3.4 Surface additives

Surface additives, such as fumed silicas are added to the toner surface to improve flow properties, transfer efficiency of the toner from the photoreceptor to paper by decreasing the adhesion of the toner to the photoreceptor, and improving the charge stability of the toner and carrier mixture. The fumed silicas also decrease the toner agglomeration.

2.1.3.5 Other additives

These additives are used in a specific application, such as silicone oil, which is used as a release agent for the fuser roll.

2.1.4 Toner Characterization

2.1.4.1 Rheology

The rheological characteristic of a toner especially affects fixing behavior. There are three significant temperatures necessary to characterize the toner fixing behavior.

a) The minimum fixing temperature is an adequate temperature at which the image is fixed to the paper.

b) The hot offset temperature is higher than the minimum fixing temperature at which the toner is so fluid that it simply splits apart when the paper leaves the fuser roll; leaving traces of the image on the fuser roll to undesirably contaminate the next sheet.

c) The blocking temperature is the temperature at which significant sintering occurs.

Besides these, a commonly measured characteristic of a polymer is its glass transition temperature, T_g, where the polymer changes from a hard glassy state to a rubbery state. This is measured in a differential scanning colorimeter, which looks for the change in heat capacity at the transition. For adequate blocking, toners generally should have a T_g value above 50° C.

2.1.4.2 Colorimetrics

For the black toner, the primary consideration is that it must generate high optical densities. For highlight color toners, there should be able to develop an optical density of the color with the tinting strength or chroma of color and pleasing hue. For process color developers, the goal is to generate as wide a color spectrum as possible, which depends on the detailed spectral absorption of various pigments.

2.1.4.3 Particle size

Toner particle sizes are generally in the range of about 10 to 20 μm in diameter. The particle sizes larger than these usually produce ragged lines and dots. The smaller particle sizes than this range improve color reproduction and noise reduction. However, the smaller particle sizes require longer times in manufacturing, hence are more expensive to produce. Also smaller sizes tend to produce more dirt at a given charge-to-mass ratio and to cause more rapid developer degradation.

2.1.4.4 Charging

The charge on the toner is controlled by the selection of its carrier chemical nature and through the mixing condition. When the toner and the carrier are rubbed together, the triboelectric series which depends on a work function of them are generated. The one lower on the work function series becomes the electron acceptor or negative charge, and the one higher on the work function series becomes the electron donor or positive charge. For the toner particle size of 10 μm, the useful range of charge-to-mass ratios is from 10 to 30 μC/g. Toner particles with a higher charge are difficult to strip from the carrier and also deposit little mass for a given amount of charge image density. The q/m values below 10 μC/g generally lead to both dirt in the machine and background density on the copy [4].

2.1.5 Current carrier powders

2.1.5.1 Carrier definition and function

Carrier is a general term in electrophotographic imaging or printing that applies when a two-component developer is used. Its most important function is to impart a static charge to the toner particles and carry the toner to the electrostatically charged images on the photoreceptor drum in the copier. [5]

2.1.5.2 Types of carrier

a) Steel (spherical)

The developer with teflon-coated spherical steel carrier, was quite insulating; consequently, the solid area reproduction was poor, and background and machine dirt have been the source of problem.

b) Iron (irregular)

Most of the iron particles are oxidized to control the resistivity and partially coated to control the electrostatic charging. For irregular powder, the high points are oxidized and poorly coated, to supply the required resistivity, while the valleys are better coated to supply the charging effect required.

c) Soft ferrites (spherical)

The resistivity of ferrite is lower than the insulating sand or glass and higher than the iron or steel. Ferrites with semiconducting properties have resistivities in the range desired, 10^6-10^{12} Ωcm, because they are transition metal oxides and magnetic ceramic materials, which in some applications can be used without partial coating for toner charging. The size range is variable, from 10-120 μm for the spherical ferrites, which are raising some interest in the industry. The spherical powder is formed by the spray drying step. The saturation magnetic moments are 20-75 electromagnetic units per gram. Too high a moment will result in a stiff brush, scratch the image, nonuniformities in the solids and ragged edges on the line copy.

d) Hard ferrites (spherical)

The commercial use of the hard or permanent magnet type of ferrite is a very recent development. In 1998, Eastman Kodak used hard ferrites for full color copiers, and gave highlights at higher speeds.

2.1.6 The two-component and single-component developments

2.1.6.1 The two-component development

This developer consists of the toner particles and the carrier beads, which provides two functions for the toner, charge generation and toner transportation through the developer housing. First, the rubbing of the carrier against the toner generates the desired magnitude and sign of charge on the toner. Second, the toner particles attach to the carrier bead by the electrostatic force and then can be moved to contact the latent image on the photoreceptor. The two-component development can be subdivided as two types, cascade development and magnetic brush development [6].

a) Cascade development

The toner of this system has an approximate diameter 10 μm particle size. They are mixed with a much larger carrier material such as glass or sand (diameter ~200-500 μm) in order to control the toner charge and transportation. In addition to control, the carrier attracts and holds the toner particles by a triboelectric interaction, which produces an electrostatic charge on the toner particles. Development of the latent image occurs as the developer flows or cascades over the surface of the dielectric material (photoreceptor) as shown in Figure 2-2. The electrostatic attraction of the latent image and the impact forces cause the toner particles to separate from the carrier and deposit on the latent image regions.

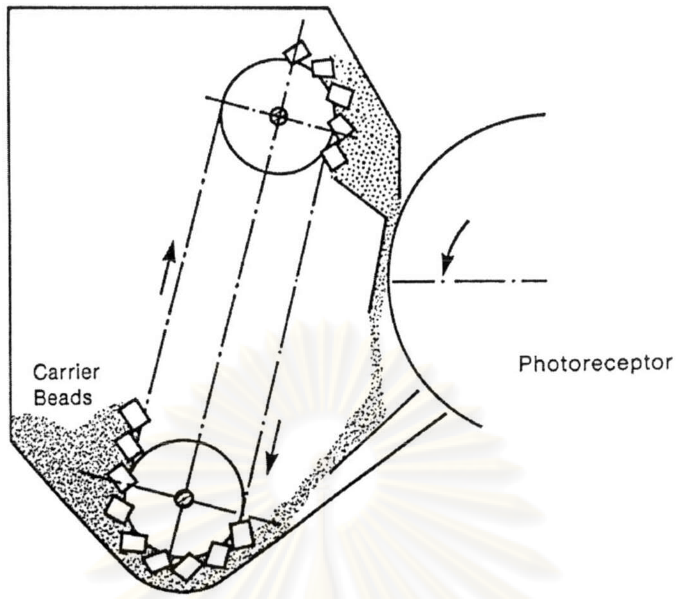

Figure 2-2 A cascade development system

b) Magnetic brush development

The toner particle size of this system is similar to that of the cascade developer. The carrier is a magnetic particle such as iron or ferrite in the size range of 50 to 200 μm. The friction between the toners and the carriers due to the magnetic field causes the carrier particles to align as bristles of a brush. These magnetic carriers bring the toner particles into contact with the latent image on the photoreceptor. A magnetic brush development system is shown in Figure 2-3.

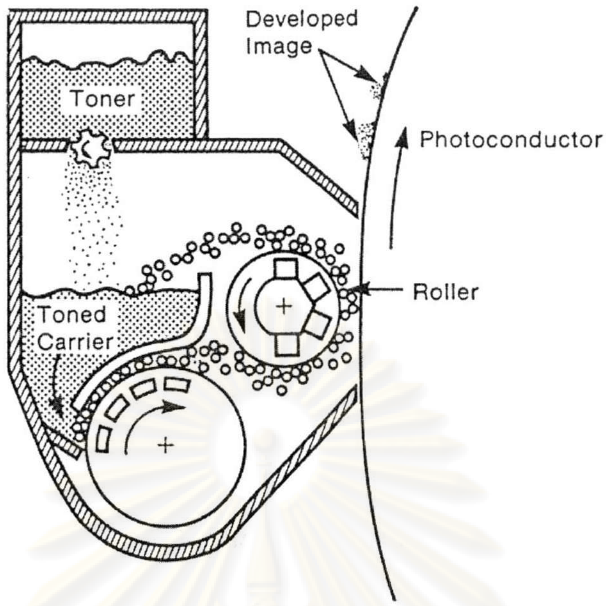

Figure 2-3 A magnetic brush development system

2.1.6.2 The single-component development

Single-component developer separates the carrier and charging functions so that only charged toner is delivered to the latent image. So, problems of carrier aging, carrier charging of the dielectric receptor and the need to control the ratio of toner to carrier are eliminated completely. The volume of developer housing, and cost can be reduced. There are two types of this toner, magnetic toner and non-magnetic toner. A typical single-component developer housing is shown in Figure 2-4 [4].

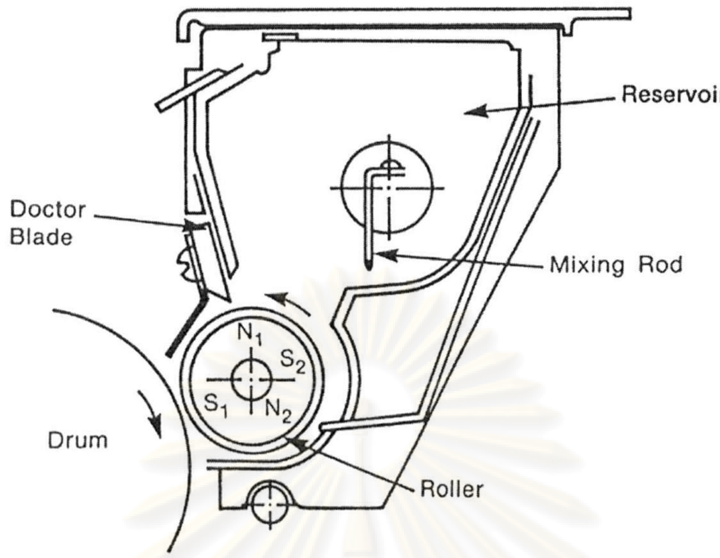

Figure 2-4 Single-component development unit

2.1.7 The charge measurement

2.1.7.1 Blow-off method

Figure 2-5 shows a blow-off method [7] that is a typical method for the two-component developer. We simply place the developer in a Faraday cage with a mesh screen on both ends. The mesh screen size ranges between the diameter of the toner and the carrier. A predetermined pressured gas (air) blows the toner particles out of the cage. The changes of the charge and mass are measured.

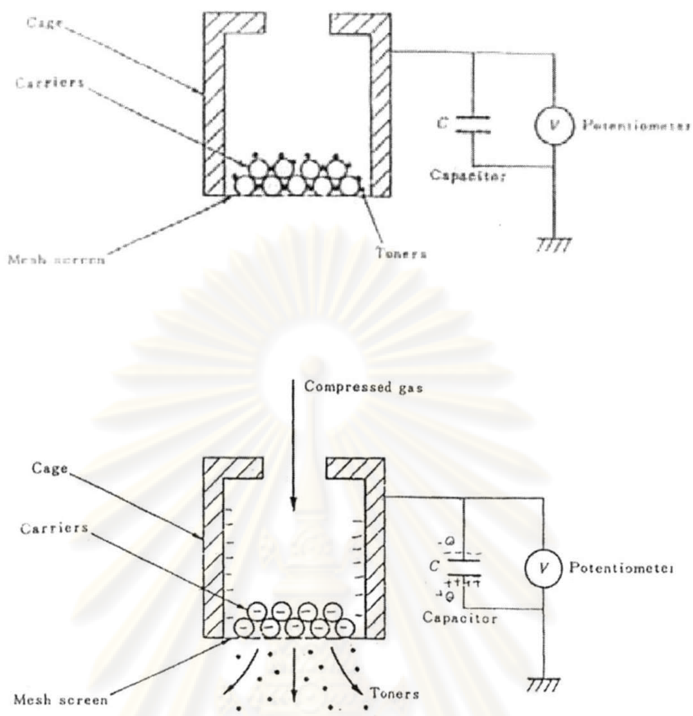

Figure 2-5 Blow-off method

2.1.7.2 E-SPART analyzer

The Electrical Single Particle Aerodynamic Relaxation Time (E-SPART) analyzer [8] is used for a real-time simultaneous measurement of aerodynamic size and electrostatic charge distribution of particles on each single particle. It simultaneously measures size in the range from submicron to 100 μm and the charge distribution from zero to saturation levels.

Its operating principle depends upon the phenomenon that when an airborne particle is subjected to an oscillatory external force, such as acoustic excitation driving field, the particles vibrate at the same frequency as the acoustic field but with a phase lag due to particle inertia. The larger the particle the greater the phase lags, which can therefore be related to particle size. To determine this phase lag, the analyzer uses a differential Laser Doppler Velocimeter (LDV) to measure the velocities of individual particles subjected to a combination of an acoustic and a DC electric field. Simultaneously a charged particle will have its vertical position shifted by the electric field by an amount related to the charge. The maximum count rate varies from 10 to 2000 particles per second depending upon particle size, which typically, can range from 0.3 μm to 75 μm.

The particles are sampled in a laminar flow field through the LDV sensing volume. As each particle passes through the sensing volume it experiences the acoustic excitation and the superimposed DC electric field in a direction perpendicular to the direction of the laminar air flow. The schematic diagram of the E-SPART analyzer is shown in Figures 2-6 to 2-8.

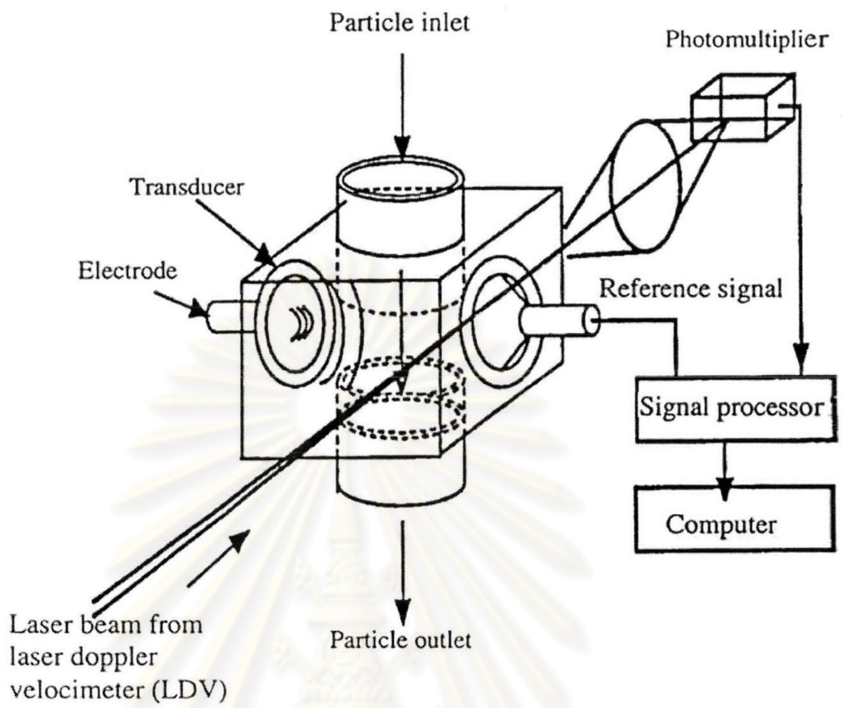

Figure 2-6 E-SPART analyzer

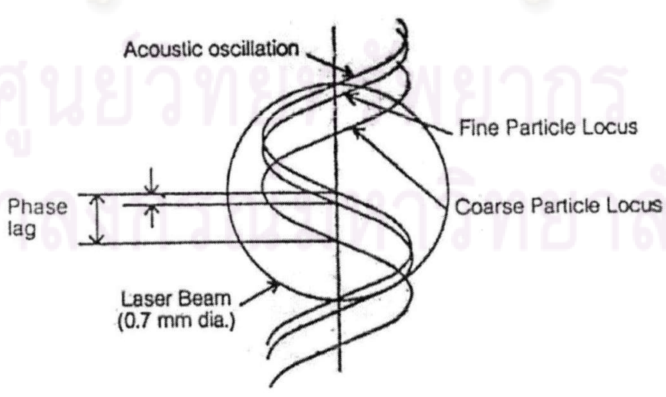

Figure 2-7 Principles for measuring particle size

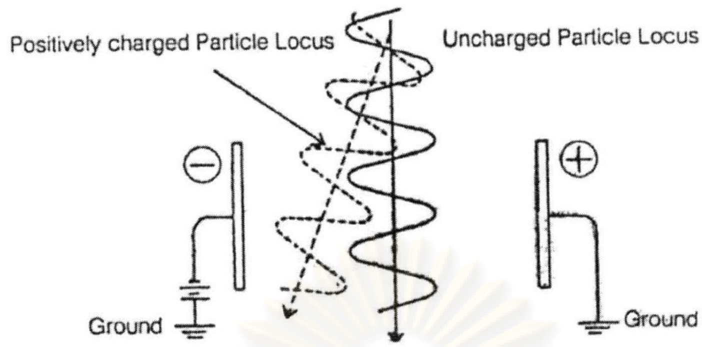

Figure 2-8 Principles for measuring electric charge of particles

2.1.8 The CIE System

The CIE colorimetric system comprises the essential standards and procedures of measurement that are necessary to make colorimetry a useful tool in science and technology. The CIE system is usually employed in connection with instruments for color measurement. This system has been established by the Commission International de I' Eclairage, the French title of international committee, or International Commission on Illumination in 1931. The CIE system started with the premise developed on the human color perception process, that stimulus for color is provided by the proper combination of a source of light, and an observer [9].

CIELAB

There are several methods of characterizing a color, including CIE L*a*b*. The CIE 1976 space, know as the CIELAB system, is the result of a mathematical transformation of the CIE 1931 system. While seeking, during this transformation, to obtain a space which is uniform in terms of color differences, one of the other objectives was to develop a much simpler system to interpret, with easier references [10]. The CIELAB space extends the tristimulus colorimetry to three-dimensional space with dimensions that approximately correlate with the perceived lightness, chroma, and hue of a stimulus [11].

The CIE 1976 (L*a*b*) color space is defined by Eqn. (3-1) to (3-3) for tristimulus values normalized to the white that are greater than 0.008856.

$$L^* = 116\,(Y/Y_n)^{1/3} - 16 \quad (3\text{-}1)$$

$$a^* = 500\,\{(X/X_n)^{1/3} - (Y/Y_n)^{1/3}\} \quad (3\text{-}2)$$

$$b^* = 200\,\{(Y/Y_n)^{1/3} - (Z/Z_n)^{1/3}\} \quad (3\text{-}3)$$

X, Y, Z are the tristimulus values of the color stimulus to be defined.

X_n, Y_n, Z_n are the tristimulus values of the reference white.

L* represents lightness

a* approximates redness-greenness

b* approximates yellowness-blueness

2.2 Literature reviews

The technology of electrophotography is applied for printers and copiers that are very widely used. The machines and materials for this system have been continually developed. Concerning the electrophotographic materials, Kamiyama et al. [1] characterized the properties of the polymerized toner and compared with those of the conventional melt-mixed toner. It was shown that the polymerized toner is more efficiently and uniformly and triboelectrically charged than is the melt-mixed toner. Its spherical shape improves fluidity and gives a smoother profile with less background fog. Next, Koyama et al. [12] studied fine-grained toner particles and developed non-spherical fine particle toner produced through an emulsion polymerization method. In this method, it is possible to inhibit dispersion stability of the emulsion polymerization particles wherein inner additives are compounded. Thereby it is possible to control the particle size so that a narrow particle size distribution is obtained, since the shape of toner particle can be freely charged and blade cleaning can be used. In addition, due to the use of emulsion polymerization particles wherein inner additives are compounded, excellent toner particle characteristics such as excellent charging property, fluidity and mechanical strength are displayed. Furthermore, Kamiyama et al. [1] described the spherical particles of the toner, which had a smooth and efficient agitation on the magnetic brush. This caused the toner particles to form a very uniform triboelectric charge. The polymerization method was used to reduce the number of manufacturing processes involved in making small particle toners. The image quality with this toner was also enhanced in the reproduction of fine lines and small dots.

In 1998, Yanagida et al. [2] developed and commercialized spherical toners by suspension polymerization as mono-component nonmagnetic toners. They compared suspension polymerized toners prepared by conventional pulverization with polymerized toners. It was shown that these polymerized toners have many superior properties than conventional pulverized toners. It is a simpler production process with a more narrow particle size distribution, higher flow-ability and transfer ratio, which has better quality of printed images and lower temperature fusing compared with encapsulated toners. Another research was reported in 2003. Kiatkamjornwong and Pomsanam [13] synthesized suspension polymerized toner in an aqueous medium and studied the physical properties, charging properties, and image quality. The resulting polymerized toners were found to be smooth on their spherical surfaces, and the particle sizes were 4-10 μm with a coefficient of variation of 20-30%. The T_g's of the resulting polymerized toners were 66-70°C. Triboelectricity of the resulting polymerized toner was 7-20 μC/g. An analysis of print quality showed high background fog, low minimum density and a small amount of image raggedness. The print result correlated with q/m values.

The triboelectric properties of two-component developer are important in practical machines, Aoike et al. [14] proposed a model for the toner tribo-charging to help explain the dependence of the toner charge on the mass ratio (q/m) of the two-component developer on the toner concentration, which was affected by the toner and the carrier properties. The carrier charge to mass ratio, q_c/m_c, to the metal plate will have different work functions, which depend on the amount of toner concentration. In the same year, Noshiro et al. [15] presented the tribo-charging behavior of two kinds of toners, which had the same composition but different shapes. Ferrite carrier was mixed with the toner. The tribo-charge of the different toners, (spherical shaped toner and irregularly shaped toner) was measured by the blow-off method. The $(q/m)_{max}$ of the irregular toner was found to be larger than that of the spherical toner at the same agitation condition. But the time constant for the charging of the irregular toner was smaller than that of the spherical toner. The time constant increased and the toner charge decreased with an increase in toner concentration of the developer. The shape factor of the toner particles was evaluated quantitatively by an image analyzer. Moreover, Kiatkamjornwong et al. [16] studied the charging properties of differently shaped toners (spherical and irregular), carrier particles that differ in their composition and surface oxide layer thickness by adjusting the applied current, and print quality. The q/m values of spherical toner were higher than the irregular toner, which produced higher densities at 60 and 40% halftones. The edge sharpness of the characters from the spherical toner was higher than those from the others. The solid densities of the different toners were close to each other. The carrier particles containing only Fe gave stronger contact with the toner than the carriers with Cu, Zn and Fe. The current on the carrier surface influenced the q/m value; the greater the friction force between two surfaces leading to the high value of q/m.

In 2002, Nakamura et al. [17] studied tribo-charging characteristics of several kinds of toner particles in two-component developer. They used the two types of negative toner samples, which were prepared by adding a negative CCA or without CCA, and one sample of positive toner was also prepared by adding a positive CCA. Two kinds of shaker were used for tribo-charging on toner with different arm lengths of 130 mm and 200 mm. Measurement of charge to mass ratio q/m was carried out by the E-SPART analyzing method. The saturation curves for the negative toner with CCA show that the q/m by tribo-charging is narrower than the negative toner without CCA. The saturation curves for the negative toner with CCA with different arm lengths show that the q/m by tribo-charging with the longer arm length of 200 mm in the shaker is obtained at a higher absolute value of 15 μC/g than that with the arm length of 130 mm. For the positive toner, the value of q/m is similar to negative toner.

Besides, there are many factors affecting the triboelectric charging. Lee et al. [18] studied the influence of charge control agent (CCA) on toner surface to toner tribo-charge. The variation of CCA materials on toner surface and toner concentration had been examined by the blow-off method. The toner q/m slightly increased as CCA content decreased. The toner q/m value was smaller for the metal including CCA than the neat CCA. The toner tribo-charge characteristics are strongly influenced by the carrier surface properties even if the toner surface properties are changed by CCA. Moreover, Poomtien et al. [19] studied charging behavior of three types of CCA at various concentrations. The presence of CCA helped increase the effectiveness of the charging sites on the toner, so that proper increase in CCA amounts increased the q/m values. The charging properties of the toners were measured by the E-SPART analyzer and blow-off measurement unit. The charging properties influenced the quality of the printed images. The toners without CCA had the lowest print density. The higher the CCA amount, the greater the print density. Very the interestingly, background density of the toners without CCA was higher than the toners with CCA. Netpradit et al. [20] investigated the dependence of the toner charge-to-mass ratio (q/m) in the two-component developer on the toner concentration (T/C), the carrier size, and the toner size in order to acquire the relationship of the print qualities, in terms of print density and the background density. The q/m values measured by the blow-off measurement showed that the toner q/m values decreased with increasing T/C. The toner charge properties, which depend on the toner resin and the carrier coating polymer are controlled by the toner size and the carrier size. A smaller toner size increased the print quality, but decreased the latitude of T/C value. A smaller carrier size gave a wider latitude of T/C with an optimum range of q/m. A low T/C value resulted in a higher toner charge, which also produced a lower print density. On the other hand, a high T/C value induced a very low toner charge and produces the very high background density.