CHAPTER II

THEORETICAL BACKGROUND

2.1 Free-Radical Polymerization[4,5]

All free-radical polymerizations have at least three basic reactions occuring simultaneously during polymerization. These include: initiation reactions continuously generate radicals during the polymerization; propagation reactions are responsible for the growth of polymer chains by monomer addition to a radical center; and biomolecular termination reactions between two radical centers give a net consumption of radicals. Free-radical may be generated by the chemical decomposition of azo and peroxide compounds, thermally and by γ-radiation. The initiation step composes of two reactions including: (a) the production of primary radicals (Eq. 2.1a), and (b) the addition of primary radicals produced to the first monomer molecule to obtain the initiating monomer species $M_1^{\bullet}$(Eq. 2.1b). The initiator (I) is usually homolytically dissociated to yield a pair of radicals $R^{\bullet}$.

$$I \xrightarrow{k_d} 2R^{\bullet} \tag{2.1a}$$

where k_d is the rate constant for the initiator dissociation.

The second reaction of the initiation can be shown as follows:

$$R^{\bullet} + M \xrightarrow{k_i} M_1^{\bullet} \tag{2.1b}$$

where M is a monomer molecule and k_I is the rate constant for the initiation step.

The propagation step consists of the growth of $M_I^{\bullet}$ by the addition of a large number of monomer molecules. Each addition creates a new radical, which has the same identity as the one previously mentioned, except that it is larger by one additional monomer unit. This step can be presented in a general term as:

$$M_n^{\bullet} + M \xrightarrow{k_p} M_{n+1}^{\bullet} \qquad (2.2)$$
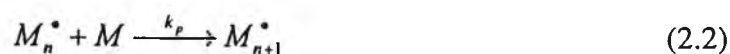
where k_p represents the propagation rate constant.

The growth of chain takes place very rapidly, the average lifetime of the growing chain is short, for instance, a chain of over 1,000 units can be produced within 10^{-2} to 10^{-3} sec. In theory, it could continuously propagate until all the monomers in the system had been consumed. If the radical concentration is high, the short chains are generally produced due to a high probability of radical interactions. The long chain polymer could be produced in the system having low radical concentration.

Termination of the growing chains may take place by the reaction of the radical centers with initiator radicals; transfer of the radical center to another molecule (such as solvent, initiator or monomer) and interaction with impurities (such as oxygen) or inhibitors. The bimolecular reaction between two radical centers is the most important termination reaction. There are the combination, which occurs by the coupling of two radical centers to form one long chain; and the disproportionation, which a hydrogen atom in a *beta* position of one radical center is abstracted by

another radical center to give a saturated polymer chain and an unsaturated polymer chain. One or both reactions may be active in any system depending on the monomer and polymerizing condition. The general term expressing the termination step is

$$M_n^* + M_m^* \xrightarrow{k_t} \text{dead polymer} \tag{2.3}$$
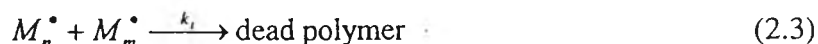
where k_t is the combination of the rate constant for the termination step.

2.2 Suspension Polymerization[6,7]

The term suspension polymerization refers to a polymerizing system in which monomer(s) is suspended as the discontinuous phase of droplets with steric stabilizers and vigorous stirring (which is maintained during polymerization) in a continuous phase. The reactor product is a slurry of suspended polymer particles. The monomers suitable for suspension polymerization usually can be polymerized by free-radical mechanisms. The continuous phase is usually water, as most monomers are relatively insoluble in water. Polymerization initiators or catalysts soluble in the monomer phase are generally used in this process. The terms pearl and bead polymerization are also used for the suspension polymerization process. The major aim in suspension polymerization is the formation of an as uniform as possible dispersion of monomer droplets in the aqueous phase with controlled coalescence of the droplets during the polymerization process. The interfacial tension, the degree of agitation, and the design of stirrer/reactor system govern the dispersion of monomer droplets. The presence of suspending agents (e.g., stabilizer) hinders the coalescence of monomer

droplets and the adhesion of partially polymerized particles during the course of polymerization, so that the solid beads may be produced in a spherical form in which the monomer was dispersed in the aqueous phase.

Several characteristics of the suspension polymerization method are common to most systems. The volume ratio of the continuous aqueous phase to the dispersed organic phase varies from 1:1 to 6:1. Higher ratios are required in rapid polymerizations, where heat is removed in a short time.[7] The bulk viscosity of the slurry is near that of water during most of the polymerizations. The low bulk fluid viscosity allows good mixing of the reactor contents at modest energy inputs and can improve heat transfer in the polymerization reactor. Water is a good medium for removing heat from polymerizing droplets because it has both a high heat capacity and a high thermal conductivity. However, suspension polymers must be seperated and dried from the water phase. Suspension droplets are not thermodynamically stable, and their coalescence is controlled by balancing the agitation system and the suspending agents. A survey of the materials used as suspending agents is given in Table 2.1.[8]

The reactor vessel is usually a stirrer tank. The monomer phase is subjected to either turbulent pressure fluctuations or viscous forces, which break it into small droplets that assume a spherical shape under the influence of interfacial tension. These droplets undergo constant collisions (collision rate ≥ 1 s^{-1}), with some of the collisions resulting in coalescence. Eventually, a dynamic equilibrium is established, leading to a stationary mean particle size. Individual drops do not retain their unique identity but undergo continuous breakup and coalescence instead. In some cases, an appropriate dispersant can be used to induce the formation of a protective film on the

droplet surface. As a result, pairs of clusters of drops that tend to coalesce are broken up the action of the stirrer before the critical coalescence period elapses. A stable state is ultimately reached in which individual drops maintain their identities over prolonged periods of time.

In the case of a polymer that is miscible in all proportions with its monomer (e.g. styrene and methyl methacrylate), a very variation of range of the dispersed phase viscosity is observed during the course of polymerization. The initially low viscosity liquid monomer is transformed gradually into an increasingly viscous polymer in monomer solution, and as conversion increases, the dispersed phase acquires the characteristics of a solid particle. Particularly in the "tacky" intermediate stage, individual polymer particles tend to form incompletely fused clumps. Agglomeration at this critical stage of conversion is somewhat inhibited by the action of the dispersant, but other effective measures to reduce coalescence may also be taken, including adjusting the densities of the two phases to make them more similar or increasing the viscosity of the aqueous continuous phase. Rapid polymerization during the sticky stage minimizes the number of effective collisions among polymer particles and thus should reduce coagulation.

The most important issue in the practical operation of suspension polymerization is the control of the final particle size distribution. The size of the particles depends on the monomer type, the viscosity change of the dispersed phase with time, the type and concentration of stabilizer, and the agitation conditions in the reactor. The locus of polymerization is the monomer/polymer beads. Due to the large size of the beads (0.1-1.0 mm), we employ the suspension polymerization rather than emulsion or the stable dispersion polymerizations. The particles must be kept suspended by agitation throughout the course of the polymerization.

Table 2.1 Materials used in suspension polymerization[8]

Suspending agents	Monomers suggested
1. Natural polymeric agents	
- Carbohydrates: starch, agar, tragacanth, pectin, plant gums such as acacia, sodium alginate	Unsaturated esters of organic acid, such as acrylate esters and vinyl esters
- Proteinaceous materials: glue, gelatin	Vinyl esters, vinyl chloride, etc.
- Alginic acid and salts	Methyl methacrylate
- Starch with buffer	Vinyl acetate
2. Modified natural polymeric agents	
- Methyl cellulose	Acrylic and vinyl eaters
- Methyl hydroxypropyl cellulose with 0.05-0.2 hydroxypropyl gr per C6 unit	Vinyl compound: vinylidene chloride, vinyl chloride, acrylonitrile, etc.
- Carboxyethyl cellulose sodium salt	Vinyl chloride
- Hydroxyethyl cellulose	Vinyl chloride
3. Synthetic polymeric agents	
(a) Containing carboxyl groups:	
- Salts of poly(acrylic acid) and of poly(methacrylic acid)	Acrylic and vinyl esters and Homologs
- Above at pH 5.5-8 with buffers	Acrylic compounds
- Sodium salts of copolymers of methacrylic acid with dichloro styrene	Dichlorostyrene, acrylonitrile, methyl methacrylate
- Salts of copolymers of maleic acid, crotonic acid, with styrene, vinyl ethers, vinyl acetate,etc.	Unsaturated, polymerizable organic compounds generally
- Salts of acrylic acid copolymers with acrylic ester or vinyl ester	Vinyl chloride, etc.
- Copolymers of maleic acid, maleic anhydride with vinyl acetate	Vinyl halides and comonomers
- Copolymers of vinyl methyl ether and maleic anhydride	Vinyl halides and comonomers
- Polymers of itaconic, fumaric, maleic, citraconic, aconitic	Vinyl compounds including
acids also partial esters or their salt	Acrylic compounds
- Sodium salts of copolymers of 1-alkoxybutadiene and maleic acid	Polymerizable vinyl compounds

Table 2.1 Materials used in suspension polymerization (continued)

Suspending agents	Monomers suggested
(b) Containing nitrogen:	
- Poly(vinyl pyrrolidone)	All polymerizable organic Compounds
- Polymeric reaction products of methyl methacrylate with ammonia	Acrylic, vinyl esters and Mixtures
- Above at pH 5.5-8 with buffers	Acrylic compounds, homologs
- Polymethacrylamide with Na_2HPO_4 and Na_2HPO_4 as buffers	Monomers in general
(c) Containing alcoholic OH groups:	
- Poly(vinyl alcohol)	Acrylic and vinyl esters
- Poly(vinyl acetate) partially saponified, mixtures of different mol. wt. and degrees of saponification	Vinyl aetate
(d) Containing sulfonic acid groups:	
- Sulfonated polystyrene with 0.15-0.5 SO_3H group per ring	Vinyl chloride with less
- Reaction products of poly(vinyl alcohol) with aldehyde sulfonic acids	Vinylidene chloride Polymerizable vinyl compounds
4. Low molecular weight compounds	
- Ester of organic hydroxyacids, e.g., octyl lactate	Polymerizable vinyl compounds Generally
- Aliphatic acid esters of poly(ethylene glycol)	Vinyl chloride
- Partial esters of polyalcohols with fatty acids, e.g., penta-etythrityl laurate	Vinyl chloride, vinylidene chloride and other vinyl compounds
- Phthalate esters	Vinyl chloride
5. Condensation polymers	
- Urea-formaldehyde	Vinyl chloride, vinylidene chloride, acrylonitrile
- Water-soluble phenol-formaldehyde	Vinyl chloride polymers

Table 2.1 Materials used in suspension polymerization (continued)

Suspending agents	Monomers suggested
6. Inorganic agents	Polymerizable vinyl and
- Powders such as kaolin, barium sulfate, talcum, aluminium, hydroxide	Vinylidene compounds
- Addition of powers produced by precipitation together with monomers	Polymerizable vinyl and Vinylidene compounds
- Tricalcium phosphate	Polymerizable vinyl and Vinylidene compounds
- Difficultly soluble neutral phosphates of 0.2-0.005 μm	Polymerizable vinyl and Vinylidene compounds
- Hydrated complex magnesium silicates	Polymerizable vinyl and Vinylidene compounds
- Bentonite (colliodal clay)	Polymerizable vinyl and Vinylidene compounds

Several other types of polymerization are carried out in aqueous medium. These must be distinguished from suspension and pearl polymerization, and they give different types of end products. An outline of these processes of polymerization is presented in Table 2.2.[8] Suspension polymerization has been used little outside the field of vinyl-type or ethylenic monomers.

Table 2.2 Polymerization processes in water[8]

Type of polymerization	Monomer solubility in water	Aqueous phase	Initiators	Place of initiator of polymerization	Polymer product	
					Molecular weight	Type of product
Solution polymerization	Water-soluble, e.g., Acrylic acid, methacrylic Acid and alkali salts; Vinyl pyrrolidone	Forms homogeneous Solution with monomers	Water-soluble, e.g., persulfates, hydrogen peroxide, hydroperoxides	In aqueous solution	Lower than in bulk polymerization	Clear, viscous, aqueous solution
Precipitation polymerization (polymer is not water soluble)	Soluble, such as acrylonitrile or less soluble, e.g., acrylic esters, vinyl acetate	Free from emulsifying and dispersing agents	Water-soluble, e.g., persulfates, hydrogen peroxide, hydroperoxides	In aqueous solution	Usually higher than in bulk polymerization (gel effect)	Water-insoluble; polymer precipitates out or forms a slurry
Emulsion polymerization	Only slightly soluble, e.g., styrene, acrylic and methacrylic esters, vinyl chloride	Emulsifying agents anionic; cationic or nonionic surfactants less common (generally 1 % or more)	Water-soluble, e.g., persulfates and peroxides; organic peroxides with redox system	In aqueous solution or in micelle surface	Higher than in bulk polymerization	Latex of fine dispersion, e.g., 0.2μ or lower particle diameters or lower particle diameter
Dispersion polymerization	Only slightly soluble, e.g., styrene, acrylic and methacrylic esters, vinyl chloride and especially vinyl acetate	High molecular, Water-soluble Polymers, e.g., poly (vinyl alcohol), poly (acrylic acid and salts)	Water-soluble persulfates, hydrogen peroxide, redox systems	In aqueous solution or in monomer droplets	Higher than in bulk polymerization when gel effect occurs	So-called polymer "emulsions", larger particle than in true latex
Peal or bead polymerization	Most slightly soluble, e.g., styrene, acrylic and methacrylic estes, vinyl chloride and especially vinyl acetate	Lower concentration of above or inorganic pulverulent agents	Monomer-soluble, e.g., benzoyl peroxide, azobisbutylonitrile	In monomer droplets	As in bulk polymerization	Spheres or granules temporarily suspended in water, easily separated

2.3 History of Electrophotography

Electrophotography is a non-impact printing, using the printer or the copier. The concept of electrophotography consisted of a photoconductor and developers. A photoconductor will be charged and subsequently discharged by the light to form an electrostatic latent image that is developed into a real visual image by attracting developers or charged toner particles. The developed image is then transferred to a paper and fused. Chester Carlson[9] first invented electrophotography in 1938 using sulfur as a photoconductive material and lycopodium powder as the original toner. Haloid Corporation[10] (now called Xerox) introduced the copier in 1959, using selenium metal as the photoconductor. The first commercial dry toners were styrene-mathacrylate polymers and had a negative electrical charge. During the 1970s IBM and Kodak[11] developed copiers, based on organic photoactive materials and positive charging toners. During the 1980s Canon and Minolta[12] started introducing low speed copiers based on selenium and cadmium sulfide photoconductors and using negative toner. Since the 1980s many combinations of single-component and two-component development and positive and negative toner have been used in the industry.

2.4 The Electrophotographic Process

The six basic steps of electrophotographic process in reproducing a copy print shown in Figure 2.1 are as follows:[13]

SHIELD | HIGH VOLTAGE CHARGE
++++++++++
(a)
CONDUCTIVE SUBSTRATE

PHOTONS
++++
(b)

TONER CARRIER
DEVELOPED MAGNETIC BRUSH
TONER
PARTICLES TONER IMAGE
(c)

PAPER
HIGH VOLTAGE
++++
+++
(d)

FUSER HEATER
(e)

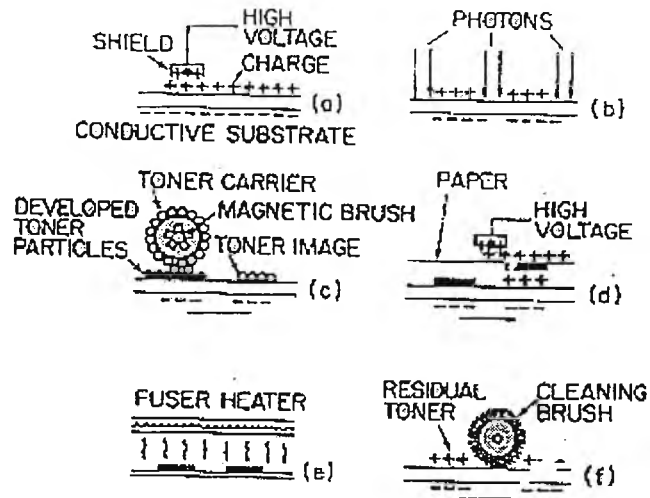RESIDUAL CLEANING
TONER BRUSH
+++
(f)

Figure 2.1 The basic steps in the electrophotographic process: (a) charging step, (b) exposure step, (c) development step, (d) transfer step, (e) fusing step, (f) cleaning step

2.4.1 Charging step, the photoconductor is covered with ions through the uses of a wire or grid biased to high voltage.

2.4.2 Exposure step, the light reflected from the white area of the original image discharges on the surface of the photoconductor, but the dark image leaves the charge and forms a latent image of charge.

2.4.3 Development step, the charged toner particles are transported to the latent image by the electric field. The negative toner is used for positive latent image on the selenium photoconductor, and the positive toner is used for negative latent image on an organic photoconductor.

2.4.4 Transfer step, a piece of substrate (paper or film) is brought into contact with the developed image on the photoconductor. The corona charging over the paper with the same polarity as the photoconductor is given to produce a large electric field between the substrate and the toner, and break the adhesive bond between the photoconductor and toner. The toner will redeposit onto the substrate.

2.4.5 Fusing step, the toner is fused into a permanent image on the paper by applying heat and/or pressure, hot roller fusing, cold pressure roll fusing, radiant fusing or flash fusing, vapor or solvent fusing.

2.4.6 Cleaning and erasing step, the photoconductor surface must be cleaned of the residual toner from the photoconductor, and the latent electrostatic image erased by an electrostatic brush, a vacuum system, or by a rubber wiper blade.

2.5 Single- and Two-Component Developers

There are two methods of charging the dry toner and transport to the latent image, that is, single- and two-component development.[13]

2.5.1 Single-component development

In a single-component development, the charged toner is brought into contact with the latent image without using a carrier, to reduce the volumn of developer housing, reduce cost and improve reliability. There are two types of the toner, magnetic toner and non-magnetic toner. The magnetic material is added to the magnetic toner, and allows magnetic forces to transport toners through the development zone to the electrostatic latent image under a magnetic control. The

commercially developing unit consists of a magnetic roll, a rotating nonmagnetic

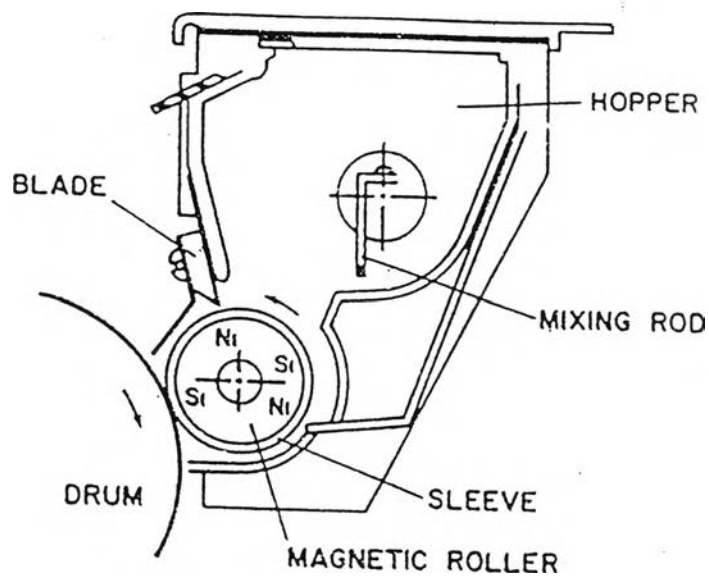donor sleeve, a magnetic blade, and a toner hopper as shown in Figure 2.2

Figure 2.2 Single-component development unit.

The magnetic roll is used to transport toners to the development zone, which is

spaced from the photoreceptor drum. The magnetic toner is triboelectrically charged

by induction and at last the opposite charge flows through the conductive toner brush

to attract the charge image of the photocunductor, as the schematic diagram in Figure

2.3. The non-magnetic toner without the magnetic material is used for a full color

printing because the magnetite is generally black and can affect the color

reproduction.

Uncharged Toner
Sleeve
Charging by induction
Charge flow through Con- ductive Toner
N Magnetic Brush
Photo- conductor
S
S
Charged Toner
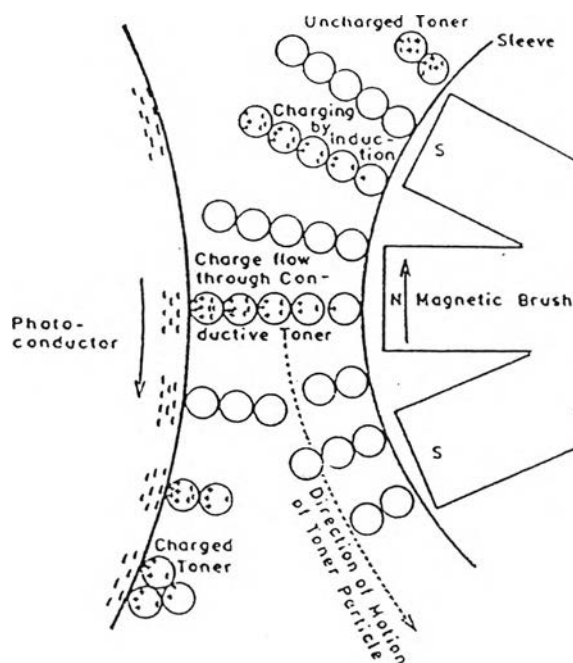Direction of Toner Particle Motion

Figure 2.3 Mechanism of development with the inductive single-component magnetic toner.

2.5.2 Two-component development

The two-component developer is the mixture of the toner and the carrier beads. There are two types of toner developments; cascade development and magnetic brush development. The cascade development was the earliest form of the two component development but it is not practical now. The carriers are too large and coarse granular of sand, glass or steel, which limited the electrode spacing, and the carrier flowed through the development zone, because the developer mixture was poured or cascaded over the photoreceptor surface. The toner particles are separated from the carrier and deposit on the latent image by the electrostatic image force agitated from rolling and bouncing. The magnetic brush development are the most

accepted technique for toner development. The carrier beads are small, 50-150 μm in diameter and fabricated from magnetic materials: iron, steel, or ferrite, with a polymer coating on the surface. The beads tend to form a bristle-like chain in the magnetic field, hence the name magnetic brush development.

The carrier provides two functions for the toner; charge generation on the toner by rubbing against the toner to generate the desired magnitude and sign of charge in the toner, and transport the toner through the developer housing. As many as 10^3 toner particles attach to each carrier bead through the electrostatic forces and transported using magnets on the magnetic carrier beads. The structure of a typical two-component development housing is shown in Figure 2.4, which consists of the toner dispenser, the paddle mixer of developers (carrier and toner), and the development magnet roll. Figure 2.5 shows a schematic development of the magnetic brush between the developer roll and the photoreceptor, while magnetic forces hold the carrier beads on the roll.
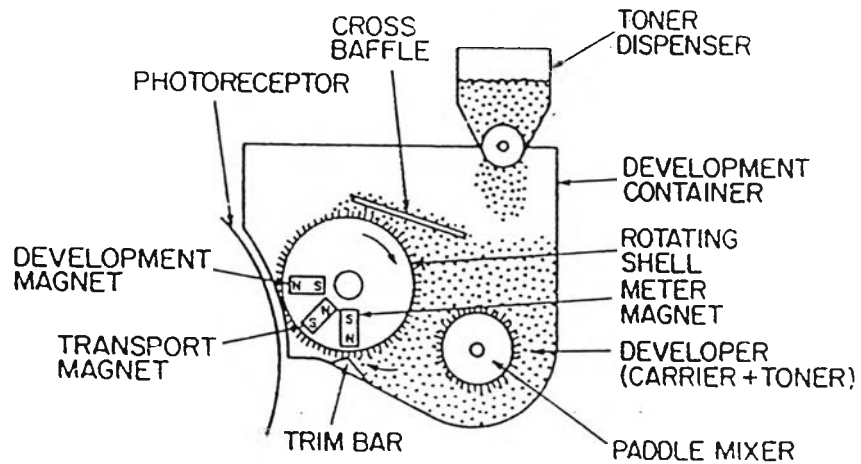
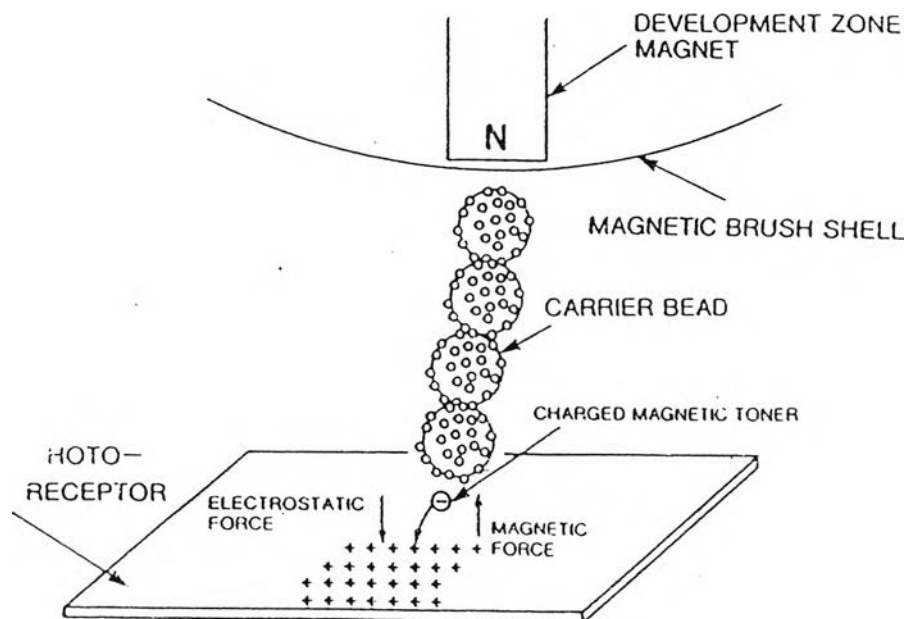Figure 2.4 Structure of a typical two component development housing.

Figure 2.5 Schematic development, indicating direction of electrostatic and magnetic

forces on toner above an image.

2.6 Toner Components

Dry electrophotographic toners consist of a colorant in a binder resin and contain charge control additives, surface additives, magnetic additives and waxes.[13]

2.6.1 Resin

The role of the resin in a toner is to bind the pigment to the paper. The thermoplastic polymer or resin is mainly used to physically fuse and fix the image to the paper by a fusing method. The primary considerations of selecting a polymer are the fusing or melting properties. There are four classes of polymers used for fabricating dry toners shown as follows:

a) Copolymers of styrenes and methacrylates or acrylates, the molecular weight ranges are 50,000-60,000 and the glass transition temperatures are 50-60°C. They are melted by heated roll and flash fusing.

b) Polyesters are of low melt viscosity and melted by radiant fusing. The molecular weight ranges are 8,000-10,000 and the glass transition temperatures are 52-54°C.

c) Epoxies, the molecular weight ranges are 1,000-10,000 and the glass transition temperatures are 60-100°C. They are melted by heated roll and flash fusing.

d) Crystalline polyethylenes or copolymer of polyethylenes, they are low molecular weight, 500-15,000, and the melting temperatures are 86-130°C. They are fixed by cold pressure, roll fusing and release agent.

2.6.2 Colorants

The carbon blacks are usually used in a black toner at a 5-15 % loading. Magnetite is used for magnetic control. Nigrosines are good black pigments and used for reduction of the carbon black. Other pigments are used in addition to blacks. The pigments are usually used in color toners, copper phthalocyanines are often used for cyans and blues, azo for yellows and quinacridones or rhodamines for magentas and reds.

2.6.3 Charge control additives

Charge control additives, CCA, are added to a toner to give an adequate charge level or rate of charging. For positive applications, the quaternary ammonium salts are used in color toner, and nigrosines are used in black toner. For negative applications, acidified carbon blacks, fumed silicas and metal complexes are used.

2.6.4 Surface additives

Surface additives, such as fumed silicas, are used to improve flow properties and transferring to paper by lowering the adhesion of the toner to the photoreceptor.

2.6.5 Magnetic additives

Magnetic additives, 60-70 % of the magnetite is added for toner transport in a single-component development, and 15-20 % of the magnetite is added for controlling machine dirt in a two-component development.

2.6.6 Other additives

Other additives, such as a release agent or silicone oil are added to prevent the adhesion of the toner to the hot roll during fusing.

2.7 Characterization of Toner[13]

2.7.1 Rheology

The rheological characteristic of a toner is affected on fixing behavior. The degree of fixing must also be sufficient to ensure durability of the copy. The fixing process, by means of heat and pressure, comprises several partial steps; sintering together of the melting toner particles, spreading the molten particles along the paper fiber, wetting the surface of the paper, penetration into the network of the paper fiber, and cooling and resetting of the toner. The following characteristics are dependent on the copolymer ratio, molecular weight, branching and crosslinking of the polymers, which are correlated to the toner fixing behavior.

a) The glass transition temperature (T_g) is the transition temperature where the polymer changes from a hard glass to a rubbery state, measured in a differential scanning colorimeter, which looks for the change in heat capacity at the transition.

b) The minimum fixing temperature $(T_{fix, min})$ is the temperature to fix the image on the paper or the degree of fixing attained at a certain level.

c) The cold offset temperature (T_{CO}) is below the minimum fix temperature at which the adhesion power between the roller surface and the toner is greater than the bonding power between the not-yet-molten toner particles on the paper.

d) The hot offset temperature (T_{HO}) is above the minimum fix temperature at which the toner is so fluid and leaves traces of the image on the fuser roll.

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

f) The fixing window, $T_{HO} - T_{CO}$, is the range of toner fixing temperature.

2.7.2 Colorimetrics

The black toners should be able to generate high optical density with practical developed masses. The highlight color toners should be able to develop an optical density of the color with the tinting strength or chroma of color and pleased hue. The process color developers (cyan, magenta, yellow and black) should generate as wide a color spectrum as possible. Each pigment is typically evaluated for lightfastness and can produce the largest gamut possible.

2.7.3 Particle size

Toner particle sizes are generally 7-12 μm in diameter. The smaller sizes have been found to improve color copy quality with noise reduction. Toner particle sizes and size distribution are measured by two techniques; the electrolytic displacement method using the Coulter counter to measure the volume size distribution of the toner, and the optical method using the E-SPART image analyzer.

2.7.4 Charging

The charge of toner is correlated to the nature of toner composition, the carrier bead coating, or the mixing condition. Triboelectric charging of toner and carrier is often determined of the work function or the position on triboelectric series of polymer. The location of the charge on a toner particle is determined in part by the

difference in energy levels between the charge exchange sites. When the toner and the carrier are contacted, the one lower on the series becomes the electron acceptor or negative charge, and the one higher on the series becomes the electron donor or positive charge. There are two quantities of the toner charge measurement:

a) Charge-to-mass ratio (q/m) by a blow-off tribo measurement is shown in Figure 2.6. This is a typical method for measuring the charge of the two-component developer. Putting the developer in a metal cage with a fine mesh screen allows the toners, but not the carrier beads, to pass through the mesh as shown in the scheme in Figure 2.7. The toner particles are blown off, and the charge and mass differences resulted are measured. The useful range of charge for 10 μm toner particles is from 10-30 μC/g. Toner charges above 30 μC/g are difficult to strip from the carrier and deposit little mass on the photoreceptor. Toner charges below 10 μC/g are difficult to control, generating machine dirt and unwanted image background on the copy.
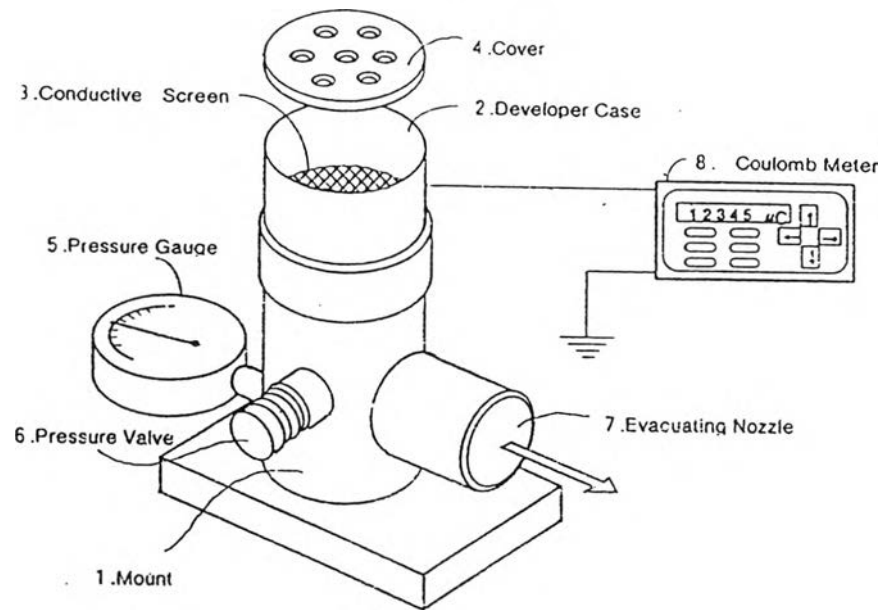
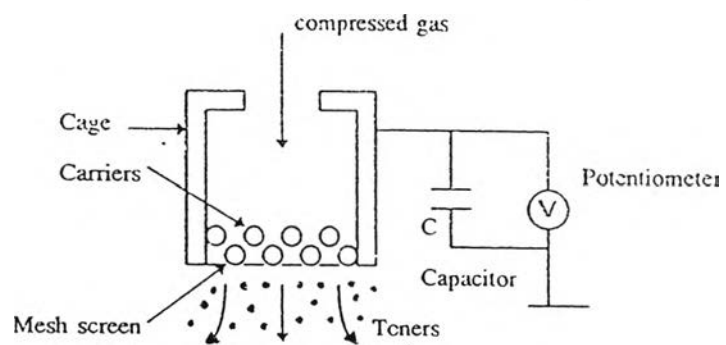Figure 2.6 Apparatus of a blow-off measurement

Figure 2.7 Conventional blow-off method

b) Charge-to-diameter ratio (q/d) by charge spectrograph measurements, a

q/d meter or an E-SPART analyzer is used for q/d measurement is shown

in Figure 2.8. This is a typical method for the single- and two-component

developers which measures the charge and diameter of toner particles

simultaneously in a single measurement with a computer analysis of the

collected filters. For the two-component developer, the toners are

separated from the carrier by the blow nozzle and fall into the toner

injection tube as shown in Figure 2.9. The q/d meter is able to measure the

distribution of charge/diameter values (fC/10μm) and the charges in

different diameter classes of developer. Most theories predict that the

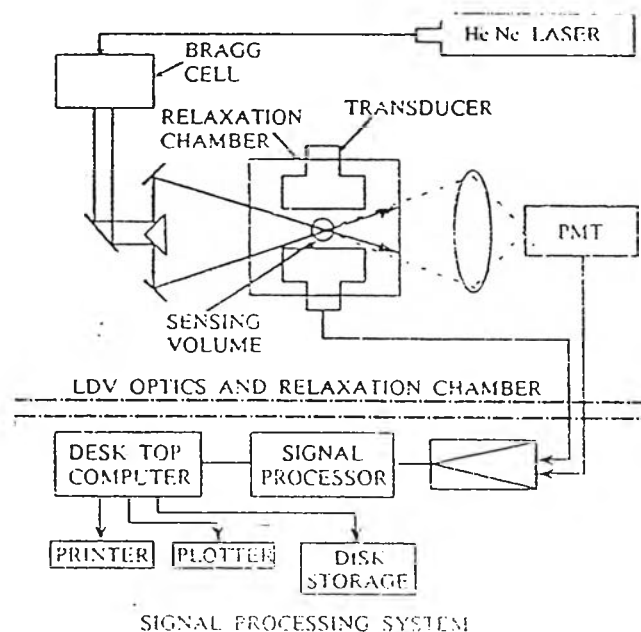charge will be proportional to the toner area.

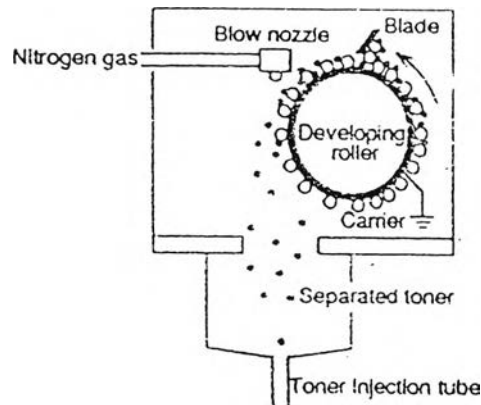Figure 2.8 Schematic diagram of an E-SPART analyzer

Figure 2.9 Method of an E-SPART analyzer

2.8 Toner Fabrication

The particle size and size distribution are parameters that can strongly influence the quality of copy, and these are in turn influenced by manufacturing techniques. Currently, there are two methods of producing commercial toners; the polymerization technique and the melt-mixing technique. The great bulk of toner is manufactured by a melt mixing method consisting of a multistep process. The pigments and internal additives with the base toner polymer are melt mixed, the temperature during the melt mixing is 80-150°C, the pigmented polymer is broken into particles of the desired size by cooling the molten toner at room temperature, and then it is rough crushed and micronized by an impact action in a high velocity air jet. The unwanted sizes are removed to give a narrower size distribution, the mixed sizes are classified to a narrow particle size distribution averaged 5-20 μm or the desired size, the small and the large particles of the toner are subjected to the attrition separate

the desired toner size by passing through the classifiers, and the narrow size toner particles are blended with the external additives.[13]

2.9 Literature Review

2.9.1 Micron-sized polymeric microsphere particles

Kamiyama et al.[14] developed a modified suspension polymerization method for generating narrow-size distribution and spherical particles in the range of 3-10 μm. In this method, both the aqueous and monomer phases are fed individually to a high speed mill where the monomer is uniformly dispersed in the aqueous solution. The system has no limitation on monomers, as long as they are compatible with suspension polymerization processes. The resulting droplets are polymerized in a separate reactor. Particles between 3-10 μm were obtained. The size of the particles was controlled by the operating parameters of the system. The particles showed excellent uniformity and the morphology was spherical in nature with smooth particle surfaces.

Winslow and Matreyek.[15] observed several suspension stabilizers, which were examined with particular emphasis on their effectiveness in providing discrete spherical particles of 0.3-0.4 mm average diameter in suspension polymerization. Poly(vinyl alcohol) was studied in greatest detail, as the various grades available allowed considerable latitude in the regulation of particle size. They found that poly (vinyl alcohol) medium solution viscosity, completely saponified not only gave the narrowest size distribution but also led to a product with a greater degree of sphericity.

Almog et al.[16] prepared micron-sized particles by breaking up monomer droplets into the micron-sized range by homogenization in the presence of a stabilizer, and subsequently, polymerized the monomer by suspension polymerization. This method prepared polymeric particles between about 50-100 μm with a wide particle size distribution because of the inherent size distribution in the mechanical homogenization step.

Barrett[17] prepared micron-sized particles with a narrow size distribution in an organic phase. The stabilizing polymers used were usually graft or block copolymers, which are used in conjunction with some quaternary ammonium salts. It was shown that the concentration of the stabilizing polymers is one of the most important factors in controlling nucleation. The number of particles increases and their size decreases as the stabilizer content is increased.

Ugelstad et al.[18] developed a method to obtain monodisperse polymeric particles of micron-sized using a two-stage swelling method, which is very efficient but very tedious and requires several reaction steps. This method was the first successful technique for preparing monodisperse polymeric particles of micron-size in the range of 0.2-1.5 μm.

Ober et al.[19] produced monodisperse copolymer particles consisting of styrene and n-butyl methacrylate in ethanol-water media. The resulting particles of 1-10 μm in the size range. It was observed that narrow size distribution could be obtained in all cases with an essential incoporation of the monomer at the feed composition. The polarity of the starting mixture as calculated from the solubility of the individual component was found to have a significant effect on final particle sizes. The more polar the reaction mixture, the smaller the final particles. Changes in the polarity of

the reaction medium with conversion of monomer to polymer was observed to broaden the particle size distribution.

2.9.2 Polymerized toner

Ochiai et al.[20] investigated the magnetic toner prepared by the suspension polymerization method. The dispersion of the magnetic powders in the toner particles was improved by hydrophobic treatment. Using the benzoyl peroxide initiator plus monomer as reagent, the magnetic powder was well dispersed. The toner improved the dispersion of the magnetic powder, which had higher electrical resistivity, and showed better electrophotographic properties.

Kamiyama et al.[21] studied the properties of the polymerized toner that are characterized and compared with those of the conventional melt-mixed toner. It was shown that the polymerized toner is more efficiently and uniformly triboelectrically charged than is the melt-mixed toner. Its spherical shape improves fluidity and gives a smoother profile with less background fog.

Yanagida et al.[22] developed and commercialized spherical toners by suspension polymerization as monocomponent 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 flowability and transfer ratio, which has better quality of printed images and lower temperature fusing compared with encapsulated toners.

Koyama et al.[23] studied fine-grained toner particles and developed nonspherical 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, 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.

Fukuda et al.[24] investigated toner with graded resin composition made by suspension polymerization technique. In the suspension polymerization of a toner composition containing a polar monomer such as MAA, the concentration of MAA is found to be higher at the surface of the toner particle. It was found that blocking resistance is improved by the addition of MAA without decreasing in fusibility, because the surface resin containing MAA has a higher glass transition temperature even if the core resin has lower one. Toner with a graded MAA concentration can be used in a low-power hot-roll fusing system, if the melting property of the core resin is controlled for fusing at lower temperatures.

Watanuki et al.[25] studied a two-component developer consisting of a magnetic toner and a magnetic carrier for a cleanerless electrophotographic process. It was found that the magnetic toner prepared by the emulsion polymerization technique exhibiting a high transfer efficiency, and the maximum transfer efficiency is nearly 100 %. Also, the small iron carrier with low resistivity has a good ability to recover the residual toner. Finally the new two-component developer allows compact page

printers to be designed without conventional cleaner units and magnetic sensors for controlling toner concentration.

2.9.3 Toner charge properties

Anderson[26] presented a model of charging for the two-component electrophotographic developer, which is based on electron donors and acceptor states on the surfaces of the carrier and the toner. If the donor and acceptor states reach an equilibrium during mixing the developer, then Fermi-Divac statistic can be used to calculate the number of charged donor and acceptor sites. The model correctly predicts the relationship between toner charge-to-mass ratio and toner concentration, toner particle size, and carrier particle size.

Schein[27] introduced the toner charge-to-mass ratio dependence on the toner concentration and charge control agent concentration in a toner-carrier mixture. The surface state theory observes the inverse dependence of the toner charge-to-mass, q/m, on toner concentration, C_t, in toner-carrier mixtures. According to this theory, a charge is exchanged between the suface states of the two materials, driven by the surface work function difference between the materials.

Akagi[28] evaluated the detachment field of charged toner particles having various sizes, composition materials and surface structures. The detachment field is dominated by the electrostatic force in the practical region of the toner charge, and the electrostatic force strongly depends on toner surface structure. The electrostatic force significantly depends on the distribution of charge over the surface of the toner particle.

Ming-Chu et al.[29] measured for the tribo-charge and the particle size distribution of the magnetic toners in a two-component developmant process. The small particle size and large q/d value of the toners can improve the print quality in image resolution and image density. The toner surface charge density is related to development efficiency in a two-component developing system. The larger toner particle size, the lower toner tribo-charge, the higher toner mass per unit area, and the toner developed on the drum surface will be increased.

Sasaki[30] presented the toner flow dynamics, simulation of changes in triboelectrific charge of developer in consideration of toner supply and consumption. The most important part of toner flow is triboelectrification, which gives significant influence to the image quality. The developing process is dependent on the triboelectric charge which is affected by the process conditions and by the charging rate, the discharging rate and the toner concentration. These factors depend on the materials of the carrier and toner. The factors which cause the triboelectric charge to deteriorate are focused on the toner adhesion to the carrier particles and the toner pulverization. The adherence of toner reduces the carrier surface area, effective to triboelectrification, resulting in a decrease in the probability of contact with toner and in maximum possible charge on toner surface (Q*). Also the pulverization of toner increases the surface area, resulting in an increase in Q*.

Anderson and Bugner[31] observed the electronic model of triboelectrification, which was applied to the two-component developer. A charge-control agent is added to the toner to control the magnitude and polarity of the electrostatic charge. As the donor energy of the charge agent decreases, the charge-to-mass of toner particles

generated by contact with a reference carrier also decreases. The acceptor energy of the charge agent over a similar range has a small effect on the charging behavior.

Lee et al.[32] studied the influence of charge control agent (CCA) in toner surface to toner tribocharge. 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 CCA, which did not include any metal. The toner tribocharge characteristics are strongly influenced by the carrier surface properties even if the toner surface properties are changed by CCA.

Aoike et al.[33] 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 is 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.

Netpradit et al.[34] 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, with 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. Smaller toner size increased the print quality, but decreased the latitude of T/C. But smaller carrier size gave a wider latitude of T/C with an optimum range of q/m. A low T/C resulted in higher toner charged, which also produced a lower print density. On the other

hand, a high T/C induced a very low toner charge and the background density was very high.

Poomtien et al.[35] studied charging behavior of three types of CCA on various concentrations. The presence of CCA helps increase the effectivity of the charging sites on the toner, so that proper increase in CCA amounts increases the q/m values. The charging properties of the toners were measured by an E-SPART analyzer and a 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 higher the print density. But, the background density of the toners without CCA were higher than the toners with CCA.

Noshiro et al.[36] presented the tribocharging behavior of two kinds of toners, which had the same composition but different shapes. Ferrite carrier was mixed with the toner. The tribocharge 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.

Kutsuwada and Nakamura[37] applied Millikan's method for the measurement of the radius and the electric charge on a singe particle. On the other hand, the Blow-off Tribocharging method cannot determine the magnitude and the sign of an electric charge on one particle of toner. The charge efficiency and the radius on a single particle of toner in the air can be determined by this apparatus. The efficiency of

electric charge of toners is nearly proportional to the third power of the radius of the toner particles, especially to the type of spherical toner. In different types of tribo charging, the quantity of electric charge of the toners is different for each charging mechanism, but there is a similar tendency for the radius of the toner particles to be dependent on the electric charge.

Baur and Macholdt[38] researched the effect of positive CCA, triphenylmethane derivatives, on charging the triboelectricity of the pure resin in sign and magnitude. With increasing numbers of SO_3H-groups, the charge control effect shifts again to the negative sign. The interaction between anion and cation has a strong influence on CCA efficiency. The efficiency of CCA itself is dominated both by chemical constitution and solid-state properties.

Kiatkamjornwong et al.[39] developed newly non-chromium containing and environmentally friendly CCAs. The CCAs based on boro-bis(1, 1'-diphenyl-1-oxo-acetyl) with difference counter ions of Li^+, Na^+, K^+ and Ca^{++} were used in the work to study their charging properties in terms of q/m value. The q/m value measurements with two E-SPART analyzers are of slightly differnce. The Coulter Counter result is higher than those of E-SPART by about 2 times. When comparing with the mono-valent ionic complex of CCA, di-valent ionic complex can generate more charges and give the higher q/m values, due to its electronic configuration and its high reactivity to polarization and ionization.

Tsunemi et al.[40] found that a low-molecular-weight type of CCA gave high surface energy toners, which induced a more hydrophilic surface. The increasing CCA content leads to increasing background density in print. The combination of a suitable polymer and an optimum CCA type and content, and the selection of readily

chargeable toner and an optimum roller material as the tribocharge donor influences an image quality.

Takahashi and Lee[41] presented that the dependency of triboelectric charging characteristics on toner concentration is governed by the relative difference of charging site numbers between toners and carriers. When the maximum number of the triboelectric charging site of carrier (N_c) is much more than the maximum number of the triboelectric charging site of toner (N_t), the triboelectric charging amount is controlled by the number of toner effective charging site only. When $N_c < N_t$, the triboelectric charging amount is controlled by the number of carrier effective charging site only. When $N_c = N_t$, the triboelectric charging amount is controlled by both the number of toner effective charging site (lower toner concentration) and the number of carrier effective charging site (higher toner concentration)

Yamamura et al.[42] indicated that the CCA has an effect on charging characteristics. They found that a saturation charge increases and the time constant of charging up decreases with the increasing CCA amount.