CHAPTER 2

EXPERIMENTAL

2.1. Materials

Styrene monomer, butyl acrylate monomer, acrylic acid and potassium persulphate of industrial grade were purchased from Mega Chemical Bhd. Laboratory reagent grade of 1-docecanethiol was bought from Fisher Scientific. Dowfax 2A1, an anionic surfactant was purchased from Dow Chemicals. Igepal CA 897, non-ionic surfactant was purchased from Rhodia Inc. All materials were directly used without further purification in the emulsion polymerization to produce the styrene-acrylate copolymer latexes.

The pigment dispersion was purchased from Clariant Corporation and wax O-307 was purchased from Nagase, Japan. The polyaluminium chloride was purchased from MayChemical. Both sodium hydroxide and aluminium chloride $AlCl_36H_2O$ of analytical reagent grade were purchased from Fisher Scientific. The benzylkonium chloride and nitric acid (65% solution in water) for analysis were bought from Acros Organic. All the materials were directly used without further purification in the emulsion-aggregation (EA) process.

2.2 Preparation of styrene-acrylate copolymer latexes

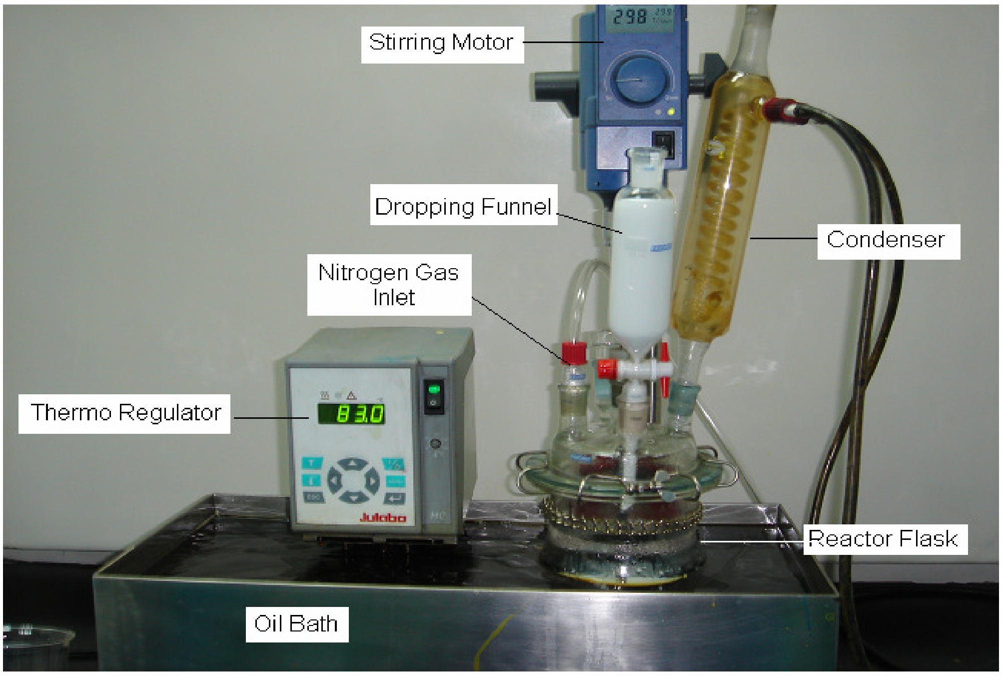

Figure 2.0: Reaction set up for emulsion polymerization

The reaction was carried out in a five-necked round bottom 1L flask fitted with a lid cover, mechanical stirrer with speed control, digital thermometer, condenser, 100 ml dropping funnel and nitrogen gas inlet as shown in Figure 2.0. Heating was carried out by an oil bath equipped with a thermo regulator to control the temperature. A series of styrene, butyl acrylate and acrylic acid copolymer latexes was synthesized by using different percentage of 1-docecanethiol, chain transfer agent (CTA) while maintaining other parameter unchanged to study the effect. The general procedure was adopted from US Patent 7041425 with slight modification [30].

Both 1.56 g of Dowfax 2A1 (anionic emulsifier) and 0.04 g of Igepal CA 897 (non-ionic emulsifier) were dissolved into 150.0 g distilled water, placed into the reactor flask and heated to 75℃. The holding flask was then purged with nitrogen gas continuously while stirring at 300 rpm maintaining the temperature at 75°C. Separately, the premix monomers emulsion and surfactants were prepared as following amount; 160.00 g styrene, 40.00 g butyl-arcylate, 3.00 g acrylic acid, 6.24 g Dowfax 2A1, 0.16 g Ipegal 897, 70.00 g distilled water and different percentage of chain transfer agent, 1-dodecanethiol (1.0, 1.4, 1.6, 1.8, 2.0 and 2.2%) were mixed and homogenized for 10 minutes at 9500 rpm using IKA Ultra-Turrax T25 Basic Homogenizer to form an emulsion. The "seed" latex was prepared by feeding in 5% of the pre-emulsion in the reactor flask containing the above aqueous surfactant phase at 75°C while being purged with nitrogen gas and allowed it to hold for 5 minutes. Meanwhile, an initiator solution of 2.00 g of potassium persulphate in 50.00 g of distilled water was prepared, and slowly charged in drop wise into the reactor and held for 20 minutes for the formation of "seed" latex. About 50% of the emulsion latex was charged in drop wise into the reactor for 2 hours (approximately 1 drop/ 3sec). Meanwhile, another initiator solution of 2.00 g potassium persulphate in 50.0 g distilled water was prepared and added drop wise into the reactor for 10 minutes after the 50% of pre-emulsion latex was fully charged in. Finally, the remaining 50% emulsion was charged in drop wise into the reactor for another 2 hours (approximately 1 drop/ 3sec). Once all the pre-emulsion was charged into reactor, the temperature was held at 75°C for an addition of 2 hours to complete the reaction. The latex was then cooled down to room temperature and was collected for the used in second part of toner making process[35-39]. The copolymer latexes were prepared in semi-continuous emulsion polymerization process according to the formulations in Table 2.0.

Table 2.0: Raw materials composition in weight (g) used to prepare copolymer latexes

Sample	**Weight of Monomers (g)**			**1-Docecanethiol as CTA**		**Dowfax 2A1 (g)**	**Igepal CA 897 (g)**	**Potassium Persulphate (g)**	**Distilled Water (g)**
	Styrene (Sty)	**Butyl Acrylate (BA)**	**Acrylic Acid (AA)**	**% (of total Sty and BA used)**	**(g)**				
E125/07	160.08	40.05	3.02	2.2	4.40	7.83	0.21	4.02	320.00
E127/07	160.05	40.00	3.00	2.0	4.02	7.84	0.22	4.00	320.09
E128/07	160.01	40.00	3.01	1.8	3.62	7.82	0.20	4.01	320.07
E129/07	160.00	40.02	3.05	1.6	3.20	7.80	0.21	4.03	320.02
E130/07	160.02	40.03	3.04	1.4	2.82	7.81	0.20	4.02	320.05
E149/08	160.00	40.00	3.02	1.0	2.01	7.80	0.21	4.03	320.10

2.3 Characterizations of copolymer latexes

2.3.1 Total Solid Contents (TSC)

The total solid content of latex is defined as the percentage by weight of non-volatile content in a system. Therefore, the solid content of the latex is according to the equation below:

$$Solid\ content\ of\ latex = \frac{Weight\ of\ polymer \times 100\,\%}{Weight\ of\ latex}$$

assuming the other materials and potassium persulphate are negligible.

The general procedure is to take a known weight of latex into an empty dish and evaporate to constant weight at 110°C temperature. If W_0 is the initial weight of sample, and the W is the weight of the residue, then the solid content is given by:

$$Total\ solid\ content = \frac{W \times 100\%}{W_o}$$

This TSC test was done with accordance to ASTM D4758-92[41] and ASTM D236993[42]. The TSC was measured directly using the latex prepared. About 2.0 g of latex was weighed (*W_o*) into an aluminum pan. The latex sample was then dried in an oven at 110˚C for 60 minutes. The dry polymer was cooled in a desiccator before it was weighted again (*W_i*). The solid content was calculated using the equation shown above.

2.3.2 Conversion of latex based on Total Solid Content

Based on total solid content (TSC) of the latex determined by gravimetric method, the monomer conversion of all the latexes were measured using the following equation below: [40-42]

$$\%\ polymer\ conversion = \frac{Experimental\ solid\ content \times 100\%}{Calculated\ solid\ content}$$

2.3.3 Particle Size Distribution (PSD)

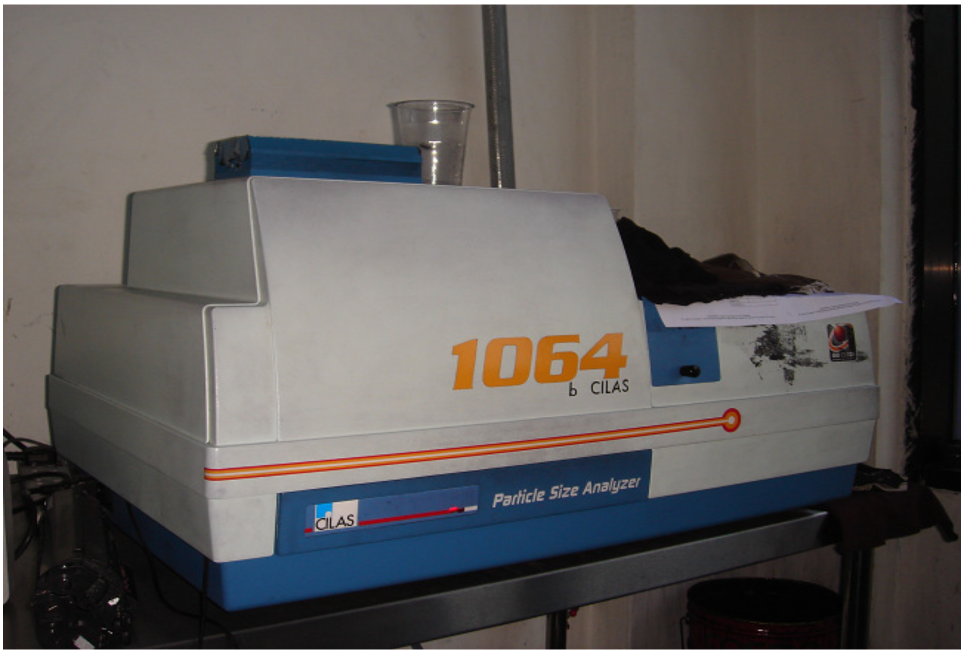

Figure 2.1: Picture of the Particle Size Analyzer

Figure 2.1 is the picture of the particle size analyzer instrument. Light scattering is the most widely used method for obtaining particle size distribution. It relies on the fact that light, when passing through a solvent or solution, loss energy by absorption, conversion to heat and scattering. When light hits small particles, the light scatters in all directions (Rayleigh scattering) as long as the particles are small compared to the wavelength (< 250 nm). If the light source is a laser, and thus is monochromatic and coherent, then one observes a time-dependent fluctuation in the scattering intensity. These fluctuations are due to the fact that the small molecules in solutions are undergoing Brownian motion and so the distance between the scattered light in the solution is constantly changing with time. This scattered light then undergoes either constructive or destructive interference by the surrounding particles and within this intensity fluctuation, information is contained about the time scale of movement of the scatterers [44-46].

The CILAS 1064L as shown in Figure 2.1 uses a laser light scattering technique with a polarized light detection system to determine sizes in the range of 0.04 to 500 µm. In practice, a few drops of emulsion latex are dispersed in water and pumped through the equipment where a laser beam is shone through a series of detectors measure the intensity of the scattered light at different angles. The background was corrected by a measurement of plain water[48].

2.3.4 Glass Transition Temperature (T_g)

Figure 2.2: Picture of the Differential Scanning Calorimeter (DSC)

Figure 2.2 is the picture of the Differential Scanning Calorimeter (DSC) instrument. Differential Scanning Calorimeter (DSC) is a thermoanalytical technique in which the difference in amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature in a specified atmosphere under a temperature program. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time.

The DSC used is the heat flux DSC type where the sample and reference are heated from the same source in the same chamber and the temperature difference, ΔT is measured as shown in Figure 2.2. This signal is converted to a power difference ΔP using the calorimetric sensitivity [49-50].

Mettler Toledo DSC 822 was used to determine the glass transition temperature (T_g) of the copolymers. The DSC was calibrated with indium standard before the actual measurement of the samples. Between 10.0 to 11.0 mg of sample was encapsulated in a non-volatile aluminium sample pan. A blank aluminium pan was used as a reference. All the samples were measured with two scannings. The first scan was carried out to erase the thermal history of the sample. After that, the instrument was allowed to cool down by itself. The results reported were from the second scan done from 25°C to the specified temperature at heating rate of 10°C /minute.

2.3.5 Molecular Weight Distribution

Figure 2.3: Picture of the Gel Permeation Chromatography (GPC)

Figure 2.3 is the picture of the Gel Permeation Chromatography (GPC) instrument. Gel permeation chromatography (GPC) is also known as size exclusion chromatography. It is a technique to determine the molecular weight distribution of a polymer sample. GPC is a particular liquid chromatography process in which the stationary phase is a porous cross-linked gel packed in chromatographic column. GPC separates the polymer according to size and hydrodynamic radius. This can be accomplished by injecting a small amount of (100-400 μl) of polymer solution (0.01-0.6%) into a set of columns that are packed with porous beads. The smaller molecules can penetrate into the pores and are therefore retained to a greater extent than the larger molecules that continue down the columns and elute faster.

Waters 1515 Isocratic HPLC Pumps and Water 2414 Refractive Index Detector as shown in Figure 2.3 were used for molecular weight distribution (MWD) determination. The machine was calibrated with polystyrene standard once a month. The instrument is purged with pure solvent for an hour before each run. The 1% w/v sample was prepared by dissolving about 0.05 g copolymer sample into 5.0 ml of filtered tetrahydrofuran (THF). When the sample was fully dissolved, 20.0 μl sample solution was injected into the column with the run time of 35 minutes [50-55].

2.3.6 Melt Flow Index (MFI)

Figure 2.4: Picture of the Melt Flow Index (MFI) Instrument

Figure 2.4 is the picture of the Melt Flow Index (MFI) instrument. Melt Flow Index (MFI) is also known as Melt Flow Rate (MFR), which measures the ease of the flow of the melted polymer. It is define as the weight of polymer in grams flowing in 10 minutes through a capillary of specific diameter and length by constant pressure applied at the prescribed temperature. The MFI can give indirect but significant measurement of the molecular weight using the equation 2.0 but this equation is only valid when the molecular weight distribution shape is invariant.

$$\frac{1}{MFR} \alpha \, M_w^{\;3.4\, to\, 3.7} \qquad \textbf{[2.0]}$$

The flow rate obtained with extrusion plastometer is not a fundamental polymer property but rather an empirically defined parameter critically influenced by the physical properties and molecular structure of the polymer and the conditions of measurement.

MFI measures the rate of extrusion of molten resin through a die of a specified length and diameter under the prescribed conditions of temperature, load and piston position in the barrel as the timed measurement is being made. The equipment consists of a cylinder, die, piston and heater like shown in Figure 2.5.

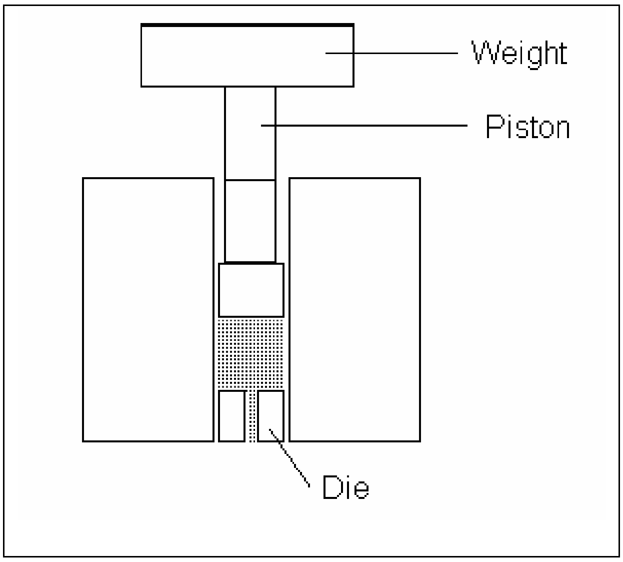

Figure 2.5: Schematic figure of a MFI machine

The steel cylinder shall be 50.8 mm in diameter, 162 mm in length with a smooth, straight hole 9.5504±0.0076 mm in diameter, displaced 4.8 mm from the cylinder axis. The outside of the steel die shall be such diameter that it will fall freely to the bottom of the hole in the cylinder. The die shall have a smooth straight bore 2.0955±0.0051 mm in diameter and shall be 8.000±0.0025 mm in length. The bore and finish critical and shall not have no visible drill or other tool marks and no detectable eccentricity. The piston shall make of steel with an insulating bushing at the top as barrier to heat transfer from the piston to the weight. The land of the piston shall be 9.4742±0.0076 mm in diameter and 6.35±0.13 mm in length. The piston have to scribed with two reference marks 4 mm apart in such fashion that when the lower mark coincides with the top of the cylinder or other suitable reference point, the bottom piston is 48 mm above the top of the die [56].

There are basically two methods to measure the MFI value which are 1) the manual cutoff operation based on time used for materials having flow rate generally between 0.15 to 50 g/10 min and 2) automatically timed flow rate measurement used for materials having flows from 0.50 to 900 g/10 min [56].

Ray-Ran Melt Flow Indexer model RR300/250 as shown in Figure 2.4 was used to perform the MFI test of the copolymers. The MFI testing was done in accordance to ASTM D 1238-94 using the automatic flow rate time method. The travel arm is adjusted to 25.40±0.25 mm. The die and the piston were inserted into the cylinder for 15 minutes before testing begun to ensure that the temperature of all these materials were stable. The piston was then removed and placed it on an insulated surface. The cylinder was charged with copolymer samples around 4.0 to 8.0 g within 1 minute and the piston was reinserted. The materials were allowed to soften and began to melt for 360 seconds with a weight support. The support was removed at such a time as to allow the test to begin within 7±0.5 mm of the completion of the charge. The timed extrudate was collected and weighted. The remainder of the specimen was discharged and pushed the die out through the top of the cylinder. Cloth patches were used to swab out the cylinder after the manner of cleaning the pistol barrel. The die may be cleaned by dissolving the residue in a solvent before proceeding to the next sample. The flow rate of all samples was calculated using equation 2.2 which was derived from the below calculation [56].

$$Flow\ rate = \frac{(427 \times L \times d)}{t}$$

where, L = length of calibrated piston travel, cm
d = density of resin at the tested temperature, g/cm^3
t = time of piston travel for length L, s
427 = mean of areas of piston and cylinder X 600

$$Flow\ rate = \frac{cm^2 \times cm \times gcm^{-3} \times 600}{t}$$

$$Flow\ rate\ (g/10\min) = \frac{weight\,(g) \times 600}{time\,(s)} \qquad \textbf{[2.2]}$$

2.4 Emulsion-aggregation process (EA Process) by varying different parameters

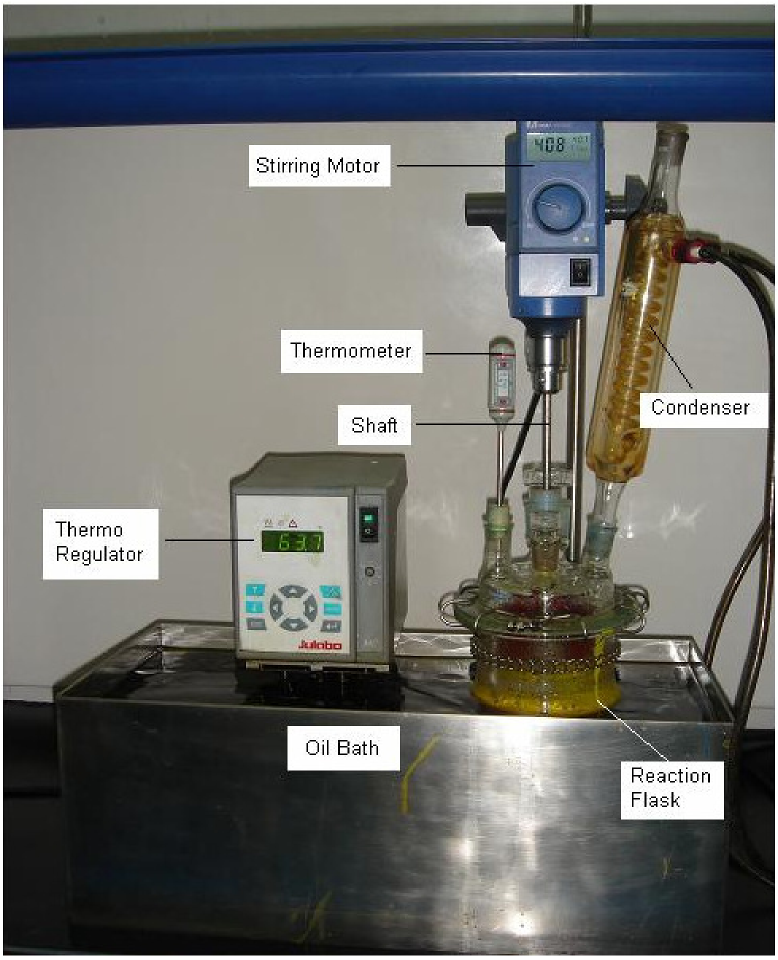

Figure 2.6: Reaction set up for emulsion-aggregation process

All the experiments were carried out in a laboratory-scale five-necked 1L flask fitted with a lid cover, mechanical stirrer with speed control, digital thermometer and condenser as shown in Figure 2.6. Heating was carried out by an oil bath equipped with a thermo regulator to control the temperature. The general procedure was adopted from US Patents 7041425 with slight modifications. Latex E125/07 was used throughout the experimental series to study on various effect on the parameters adjusted before finalizing on the best parameter used in the final stage of producing the finished toner for test printing performance. In the final stage where the raw toner produced was used to proceed to the blending stage, experiments were carried out by using blended latex of E130/07 and E149/08 in the ratio of 50:50 which gives better properties than using latex E125/07 alone [30-35].

For all the emulsion-aggregation experiments, the raw materials used were calculated based on the yield to produce 60.0 g dried weight of raw toner after drying. The calculation made is based on the solid content of the raw materials and the percentage of dried weight required in the final product. The calculation of the exact weight used is shown below. The total solid content, percentage of dried weight and amount used is tabulated in Table 2.1.

$$
\begin{aligned}
&Solid\ content\ of\ latex = 38.04\% \\
&Percentage\ of\ re\sin\ needed = 87.0\% \\
&Amount\ of\ re\sin\ used\ to\ product\ 60.0\ g\ raw\ toner \\
&= \frac{(87\% \times 60.0\ g) \times 100}{38.04} \\
&= 138.01\ g
\end{aligned}
$$

$$
\begin{aligned}
&Solid\ content\ of\ pigment\ dispersion = 20.0\% \\
&Percentage\ of\ dried\ pigment\ needed = 5.0\% \\
&Amount\ of\ pigment\ dispersion\ used\ to\ produce\ 60.0\ g\ raw\ toner \\
&= \frac{(15.0\% \times 60.0\ g) \times 100}{20.00} \\
&= 15.0\ g
\end{aligned}
$$

$$\begin{aligned}&\text{Solid content of wax dispersion} = 35.0\%\\&\text{Percentage of dried wax needed} = 8.0\%\\&\text{Amount of wax dispersion used to produce } 60.0\ g \text{ raw toner}\\&= \frac{(8.0\% \times 60.0\ g) \times 100}{35.00}\\&= 13.7\ g\end{aligned}$$

Table 2.1: The TSC, percentage dried weight and amount used of the raw materials used

Raw Materials	**Total Solid Content (TSC) (%)**	**% of dried weight**	**Amount used (g)**
Latex	38.40	87.0	138.01
Wax Dispersion	35.00	5.0	15.0
Pigment Dispersion	20.00	8.0	13.7
		100.0	

A few series of emulsion-aggregation experiments were carried out with varying of different parameters in order to study their effects on the toner properties as shown in Table 2.2. Most series were carried out up to 5 experiment variables but some series were stopped after 3 experiment variables because the properties had already exceeded the required specifications at the third case.

Table 2.2: The series of experiments that had been carried out

Series	**Experiment variables carried out**
I	Different PAC amount **(1.4, 1.8, 2.0, 2.5 and 3.0 g)**
II	Different aggregation pH **(pH 1.0, 2.5 and 3.0)**
III	Different aggregation time **(2, 3, 4, 5 and 6 hours)**
IV	Different coalescences pH **(pH 6, 7 and 8)**
V	Different coalescences temperature **(80, 90 and 95°C)**
VI	Different amount of benzylkonium chloride **(0.0, 0.05, 0.07, 0.10 and 0.15 g)** used with 2.0g of PAC.
VII	Different percentage of wax **(6, 7 and 8%)**
VIII	Latexes prepared using different percentage of CTA **(1.0, 1.4, 1.6, 1.8, 2.0, and 2.2%)**

2.4.1 Different amount of PAC

The materials and compositions of the reaction mixtures were shown in Table 2.3. Latex E125/07 of dried solid content 38.04% and aqueous Clariant pigment dispersion (Carbon Black, Yellow, Cyan or Magenta) of dry solid content of 20.0% were simultaneously added to the distilled water with high shear stirring by means of IKA Ultra-Turrax T25 Basic Homogenizer for 5 minutes. After that, the O-307 wax dispersion with dry solid content of 35.0% was added into the mixture with continuous high shear stirring for another 5 minutes. To this mixture, the polyaluminium chloride (PAC) 10% w/v of different amount (1.4, 1.8, 2.0, 2.5 and 3.0 g) in 10.0 g 0.2M nitric acid was added over a period of 3 minutes with continuous homogenizing at speed of 9500 rpm for a period of 5 minutes. The resulting mixture pH was adjusted to 3 before it was transferred to a 1L reactor flask and heated to 57°C. The aggregation process was carried out for 4 hours. The pH of the mixture was then adjusted from pH 2.2 to pH 8.0 with a base solution of 4% sodium hydroxide. Subsequently, the mixture was heated from 57°C to 90°C and the pH of the mixture was adjusted back from pH 7.2 to pH 6 using 0.2 M nitric acid. The coalescences process was retained for a period of 3 hours before cooling down to room temperature.

The resulting wet cake toner was stirred in 1L of distilled water for 60 minutes for washing and isolated by filtration. The process was repeated for 4 times and the wet cake was dried in a vacuum oven. The final raw toner product comprised of 87% resin, 5% pigment and 8% wax assuming the amount of PAC used is negligible.

Table 2.3: Raw materials composition in weight (g) used for series I

Ingredients	% of dried weight	Amount Used (g)
Resin	87	138.01
Pigment Dispersion	5	15.0
Wax Dispersion	8	13.7
Polyaluminium chloride (PAC)	-	**1.4, 1.8, 2.0, 2.5 and 3.0**
Distilled Water	-	280.35

2.4.2 Different aggregation pH

The materials and compositions of the reaction mixtures were shown in Table 2.4. Latex E125/07 of dried solid content 38.04% and aqueous Clariant pigment dispersion (Carbon Black, Yellow, Cyan or Magenta) of dry solid content of 20.0% were simultaneously added to the distilled water with high shear stirring by means of IKA Ultra-Turrax T25 Basic Homogenizer for 5 minutes. After that, the O-307 wax dispersion with dry solid content of 35.0% was added into the mixture with continuous high shear stirring for another 5 minutes. To this mixture, 2.0g the polyaluminium chloride (PAC) 10% w/v in 10.0 g 0.2 M nitric acid was added over a period of 3 minutes with continuous homogenizing at speed of 9500 rp m for a period of 5 minutes. The pH of the resulting mixture was adjusted to differ pH (pH 1.0, 2.5 and 3.0) before it was transferred to a 1L reactor flask and heated to 57°C. The aggregation process was carried out for 4 hours. The pH of the mixture was then adjusted from pH 2.2 to pH 8.0 with a base solution of 4% sodium hydroxide. Subsequently, the mixture was heated from 57°C to 90°C and the pH of the mixture was adjusted back from pH 7.2 to pH 6 using 0.2 M nitric acid. The coalescences process was retained for a period of 3 hours before cooling down to room temperature.

The resulting wet cake toner was stirred in 1L of distilled water for 60 minutes for washing and isolated by filtration. The process was repeated for 4 times and the wet cake was dried in a vacuum oven. The final raw toner product comprised of 87% resin, 5% pigment and 8% wax assuming the amount of PAC used is negligible.

Table 2.4: Raw materials composition in weight (g) used for series II

Ingredients	**% of dried weight**	**Amount Used (g)**
Resin	87	138.01
Pigment Dispersion	5	15.0
Wax Dispersion	8	13.7
Polyaluminium chloride (PAC)	-	2.0
Distilled Water	-	280.35

2.4.3 Different aggregation time

The materials and compositions of the reaction mixtures were summarized in Table 2.5. Latex E125/07 of dried solid content 38.04% and aqueous Clariant pigment dispersion (Carbon Black, Yellow, Cyan or Magenta) of dry solid content of 20.0% were simultaneously added to the distilled water with high shear stirring by means of IKA Ultra-Turrax T25 Basic Homogenizer for 5 minutes. After that, the O-307 wax dispersion with dry solid content of 35.0% was added into the mixture with continuous high shear stirring for another 5 minutes. To this mixture, 2.0 g of the polyaluminium chloride (PAC) 10% w/v in 10.0 g 0.2 M nitric acid was added over a period of 3 minutes with continuous homogenizing at speed of 9500 rpm for a period of 5 minutes. The resulting mixture pH was adjusted to 3 before it was transferred to a 1L reactor flask and heated to 57°C. The aggregation process was carried out for (2, 3, 4, 5 and 6 hours). The pH of the mixture was then adjusted from pH 2.2 to pH 8.0 with a base solution of 4% sodium hydroxide. Subsequently, the mixture was heated from 57°C to 90°C and the pH of the mixture was adjusted back from pH 7.2 to pH 6 using 0.2 M nitric acid. The coalescences process was retained for a period of 3 hours before cooling down to room temperature.

The resulting wet cake toner was stirred in 1L of distilled water for 60 minutes for washing and isolated by filtration. The process was repeated for 4 times and the wet cake was dried in a vacuum oven. The final raw toner product comprised of 87% resin, 5% pigment and 8% wax assuming the amount of PAC used is negligible.

Table 2.5: Raw materials composition in weight (g) used for series III

Ingredients	% of dried weight	Amount Used (g)
Resin	87	138.01
Pigment Dispersion	5	15.0
Wax Dispersion	8	13.7
Polyaluminium chloride (PAC)	-	2.0
Distilled Water	-	280.35

2.4.4 Different coalescences pH

The materials and compositions of the reaction mixtures were shown in Table 2.6. Latex E125/07 of dried solid content 38.04% and aqueous Clariant pigment dispersion (Carbon Black, Yellow, Cyan or Magenta) of dry solid content of 20.0% were simultaneously added to the distilled water with high shear stirring by means of IKA Ultra-Turrax T25 Basic Homogenizer for 5 minutes. After that, the O-307 wax dispersion with dry solid content of 35.0% was added into the mixture with continuous high shear stirring for another 5 minutes. To this mixture, 2.0 g of the polyaluminium chloride (PAC) 10% w/v of different amount in 10.0 g 0.2M nitric acid was added over a period of 3 minutes with continuous homogenizing at speed of 9500 rpm for a period of 5 minutes. The resulting mixture pH was adjusted to 3 before it was transferred to a 1Lp reactor flask and heated to 57°C. The aggregation process was carried out for 4 hours. The pH of the mixture was then adjusted from pH 2.2 to pH 8.0 with a base solution of 4% sodium hydroxide. Subsequently, the mixture was heated from 57°C to 90°C and the pH of the mixture was adjusted back from pH 7.2 to (6, 7 and 8) using 0.2 M nitric acid. The coalescences process was retained for a period of 3 hours before cooling down to room temperature.

The resulting wet cake toner was stirred in 1L of distilled water for 60 minutes for washing and isolated by filtration. The process was repeated for 4 times and the wet cake was dried in a vacuum oven. The final raw toner product comprised of 87% resin, 5% pigment and 8% wax assuming the amount of PAC used is negligible.

Table 2.6: Raw materials composition in weight (g) used for series IV

Ingredients	% of dried weight	Amount Used (g)
Resin	87	138.01
Pigment Dispersion	5	15.0
Wax Dispersion	8	13.7
Polyaluminium chloride (PAC)	-	2.0
Distilled Water	-	280.35

2.4.5 Different coalescence temperature

The materials and compositions of the reaction mixtures were shown in Table 2.7. Latex E125/07 of dried solid content 38.04% and aqueous Clariant pigment dispersion (Carbon Black, Yellow, Cyan or Magenta) of dry solid content of 20.0% were simultaneously added to the distilled water with high shear stirring by means of IKA Ultra-Turrax T25 Basic Homogenizer for 5 minutes. After that, the O-307 wax dispersion with dry solid content of 35.0% was added into the mixture with continuous high shear stirring for another 5 minutes. To this mixture, 2.0 g of the polyaluminium chloride (PAC) 10% w/v in 10.0 g 0.2 M nitric acid was added over a period of 3 minutes with continuous homogenizing at speed of 9500rpm for a period of 5 minutes. The resulting mixture pH was adjusted to 3 before it was transferred to a 1L reactor flask and heated to 57°C. The aggregation process was carried out for 4 hours. The pH of the mixture was then adjusted from pH 2.2 to pH 8.0 with a base solution of 4% sodium hydroxide. Subsequently, the mixture was heated from 57°C to (80, 90 and 95°C) and the pH of the mixture was adjusted back from pH 7.2 to pH 6 using 0.2 M nitric acid. The coalescences process was retained for a period of 3 hours before cooling down to room temperature.

The resulting wet cake toner was stirred in 1L of distilled water for 60 minutes for washing and isolated by filtration. The process was repeated for 4 times and the wet cake was dried in a vacuum oven. The final raw toner product comprised of 87% resin, 5% pigment and 8% wax assuming the amount of PAC used is negligible.

Table 2.7: Raw materials composition in weight (g) used for series V

Ingredients	% of dried weight	Amount Used (g)
Resin	87	138.01
Pigment Dispersion	5	15.0
Wax Dispersion	8	13.7
Polyaluminium chloride (PAC)	-	2.0
Distilled Water	-	280.35

2.4.6 Different amount of benzylkonium chloride used with 2.0g PAC

The materials and compositions of the reaction mixtures were shown in Table 2.8. Latex E125/07 of dried solid content 38.04% and aqueous Clariant pigment dispersion (Carbon Black, Yellow, Cyan or Magenta) of dry solid contents of 20.0% were simultaneously added to the distilled water with high shear stirring by means of IKA Ultra-Turrax T25 Basic Homogenizer for 5 minutes. After that, the O-307 wax dispersion with dry solid contents of 35.0% was added into the mixture with continuous high shear stirring for another 5 minutes. To this mixture, 2.0 g the polyaluminium chloride (PAC)

10% w/v in 10.0 g 0.2 M nitric acid was added over a period of 3 minutes followed by different amount of addition of benzylkonium chloride (0.00, 0.05, 0.07, 0.10 and 0.15 g) with continuous homogenizing at speed of 9500 rpm for a period of 5 minutes. The resulting mixture pH was adjusted to 3 before it was transferred to a 1L reactor flask and heated to 57°C. The aggregation process was carried out for 4 hours. The pH of the mixture was then adjusted from pH 2.2 to pH 8.0 with base solution of 4% sodium hydroxide. Subsequently, the mixture was heated from 57°C to 90°C and the pH of the mixture was adjusted back from pH 7.2 to pH 6 using 0.2 M nitric acid. The coalescences process was retained for a period of 3 hours before cooling down to room temperature.

The resulting wet cake toner was stirred in 1L of distilled water for 60 minutes for washing and isolated by filtration. The process was repeated for 4 times and the wet cake was dried in a vacuum oven. The final raw toner product comprised of 87% resin, 5% pigment and 8% wax assuming the amount of PAC and benzylkonium chloride used are negligible.

Table 2.8: Raw materials composition in weight (g) used for series VI

Ingredients	**% of dried weight**	**Amount Used (g)**
Resin	87	138.01
Pigment Dispersion	5	15.0
Wax Dispersion	8	13.7
Polyaluminium chloride (PAC)	-	2.0
Benzylkonium Chloride	-	**0.00, 0.05, 0.07, 0.10, 0.15**
Distilled Water	-	280.35

2.4.7 Different percentage of wax

The materials and compositions of the reaction mixtures were shown in Table 2.9. Latex E125/07 of dried solid content 38.04% and aqueous Clariant pigment dispersion (Carbon Black, Yellow, Cyan or Magenta) of dry solid contents of 20.0% were simultaneously added to the distilled water with high shear stirring by means of IKA Ultra-Turrax T25 Basic Homogenizer for 5 minutes. After that, the O-307 wax dispersion of **(6, 7 and 8%)** with dry solid contents of 35.0% was added into the mixture with continuous high shear stirring for another 5 minutes. To this mixture, 2.0 g of the polyaluminium chloride (PAC) 10% w/v in 10.0 g 0.2 M nitric acid was added over a period of 3 minutes followed with continuous homogenizing at speed of 9500 rpm for a period of 5 minutes. The resulting mixture pH was adjusted to 3 before it was transferred to a 1L reactor flask and heated to 57°C. The aggregation process was carried out for 4 hours. The pH of the mixture was then adjusted from pH 2.2 to pH 8.0 with a base solution of 4% sodium hydroxide. Subsequently, the mixture was heated from 57°C to 90°C and the pH of the mixture was adjusted back from pH 7.2 to pH 6 using 0.2 M nitric acid. The coalescences process was retained for a period of 3 hours before cooling down to room temperature.

The resulting wet cake toner was stirred in 1L of distilled water for 60 minutes for washing and isolated by filtration. The process was repeated for 4 times and the wet cake was dried in a vacuum oven. The final raw toner product comprised of 87 % to 89 % resin, 5 % pigment and 6 %, to 8% wax assuming the amount of PAC used is negligible.

Table 2.9: Raw materials composition in weight (g) used for series VII

Ingredients	% in dried raw toner	Amount Used (g)
Resin	**87, 88 and 89**	**138.01, 138.80 and 140.38**
Pigment	5	15.0
Wax	**8, 7 and 6**	**13.70, 11.99 and 10.28**
Polyaluminium chloride (PAC)	-	2.0
Distilled Water	-	280.35

2.4.8 Different percentage of chain transfer agent latexes

The materials and compositions of the reaction mixtures were shown in Table 2.10. Latexes of different percentage of 1-dodecanethiol, chain transfer agent (1.0, 1.4, 1.6, 1.8, 2.0, and 2.2%) and aqueous Clariant pigment dispersion (Carbon Black, Yellow, Cyan or Magenta) of dry solid contents of 20.0% were simultaneously added to the distilled water with high shear stirring by means of IKA Ultra-Turrax T25 Basic Homogenizer for 5 minutes. After that, the O-307 wax dispersion with dry solid contents of 35.0% was added into the mixture with continuous high shear stirring for another 5 minutes. To this mixture, 2.0 g of the polyaluminium chloride (PAC) 10% w/v in 10.0 g 0.2 M nitric acid was added over a period of 3 minutes with continuous homogenizing at speed of 9500 rpm for a period of 5 minutes. The resulting mixture pH was adjusted to 3 before it was transferred to a 1L reactor flask and heated to 57°C. The aggregation process was carried out for 4 hours. The pH of the mixture was then adjusted from pH 2.2 to pH 8.0 with a base solution of 4% sodium hydroxide. Subsequently, the mixture was heated from 57°C to 90°C and the pH of the mixture was adjusted back from pH 7.2 to pH 6 using 0.2 M nitric acid. The coalescences process was retained for a period of 3 hours before cooling down to room temperature.

The resulting wet cake toner was stirred in 1L of distilled water for 60 minutes for washing and isolated by filtration. The process was repeated for 4 times and the wet cake was dried in a vacuum oven. The final raw toner product comprised of 87% resin, 5% pigment and 8% wax assuming the amount of PAC used is negligible.

Table 2.10: Raw materials composition in weight (g) used for series VIII

Ingredients		**% of dried weight**	**Amounts Used (g)**
Latex	**% CTA used**		
E125/07	2.2	87	137.22
E127/07	2.0		137.19
E128/07	1.8		137.22
E129/07	1.6		137.59
E130/07	1.4		137.44
E149/08	1.0		137.88
Pigment Dispersion		5	15.0
Wax Dispersion		8	13.7
Polyaluminium chloride (PAC)		-	2.0
Distilled Water		-	280.35

2.5 Characterization of raw toner and finished toner

The dried toner powder after the emulsion-aggregation (EA) is known as the raw toner. The raw toner will then undergo additives blending before packing into the cartridges. Toner after additive blending and packed into the cartridges is known as the finished toner. The finished toner is the final product that can be used in the laser printer.

2.5.1 Particle Size Distribution (PSD)

In practice, about 3.0 g of raw toner are dispersed in water and pumped through the equipment where a laser beam is shone through a series of detectors measure the intensity of the scattered light at different angles. The spectrum will show the particle size distribution of the sample. (Appendix A)

2.5.2 Glass Transition Temperature (T_g)

Mettler Toledo DSC 822 was used to measure the glass transition temperature (T_g) of the raw toners. The equipment was calibrated with indium standard before actual measurement of the samples. Between 10.0 mg to 11.0 mg of sample was encapsulated in a non-volatile aluminium sample pan. A blank aluminium pan was used as a reference. All the samples were measured with two scannings. The first scan was carried out to erase the thermal history of the sample. After that, the instrument was allowed to cool down by itself. The results reported were from the second scan done from 25°C to the specified temperature at heating rate of 10°C /minute. (Appendix B)

2.5.3 Wax Content and Wax Melting Point (T_p)

Besides, measuring the glass transition temperature of the toner, the Mettler Toledo DSC 822 can be used to estimate the wax content as well as the wax melting point of the raw toners. Between 10.0 mg to 11.0 mg of sample was encapsulated in a non-volatile aluminium sample pan. A blank aluminium pan was used as a reference. All the samples were measured with two scannings. The first scan was carried out to erase the thermal history of the sample. After that, the instrument was allowed to cool down by itself. The results reported were from the second scan done from 25°C to the specified temperature at heating rate of 10°C /minute.

The delta value (entalphy of fussion) of the wax was obtained by running the pure O-307 wax. From the spectrum, the delta obtained was 209.99 Jg^{-1} which is near to 210.0 Jg^{-1}. Thus, all the delta value used to obtain the wax content was 210.0 Jg^{-1}. The spectrum to obtain the delta value (entalphy of fussion) for the wax is shown in the Appendix C.

2.5.4 Molecular Weight Distribution

Waters 1515 Isocratic HPLC Pumps and Water 2414 Refractive Index Detector were used for molecular weight distribution measurement. The machine was calibrated with polystyrene standard once a month because the machine is still very new. It is allowed to purge about one hour to stabilize the machine before each run. The 1% w/v sample was prepared by dissolving about 0.0500 g raw toner sample into 5.0 ml of filtered tetrahydrofuran (THF). When the sample was fully dissolved, 20.0 μl sample solution was injected into the column with the run time of 35 minutes. (Appendix D)

2.5.5 Melt Flow Index (MFI)

The MFI testing was done in accordance to ASTM D 1238-94. The travel arm is adjusted to 25.40±0.25 mm. The die and the piston were inserted into the cylinder for 15 minutes before testing begun to ensure that the temperature of all these materials were stable. The piston was then removed and placed it on an insulated surface. The cylinder was charged with raw toner samples around 4.0 to 8.0 g within 1 minute and the piston was reinserted. The materials were allowed to soften and began to melt for 360 seconds with a weight support. The support was removed at such a time as to allow the test to begin within 7±0.5 mm of the completion of the charge. The timed extrudate was collected and weighted. The remainder of the specimen was discharged and pushed the die out through the top of the cylinder. Cloth patches were used to swab out the cylinder after the manner of cleaning the pistol barrel. The die may be cleaned by dissolving the residue in a solvent before proceeding to the next sample [56].

2.5.6 Tribocharge

Figure 2.7: Picture of the triboelectric instrument

The triboelectric effect is a type of contact electrification in which certain materials become electrically charged after they come into contact with another different material and are then separated (such as through rubbing). The polarity and strength of the charged produced differ according to all the materials, surface roughness, temperature, strain and other properties.

The technique used in determining the tribocharge value for toners is the standard “blow off” method as shown in Figure 2.7. The tribocharge testing was done in accordance to ASTM F1425-06. This test method measures a fundamental property of a toner and developer mix used in copiers and printers [57].

Exactly 0.10 g sample and 2.00 g of carrier (part of the measuring instrument) were weighted into the known weighted cell which has a screen opening that is large enough for the toner but not the carrier to pass through. The toner is blown off using the dry compressed air of approximately 2.76×10^5 Pa. The result was recorded on the charge remaining on the carrier opposite in the polarity to the blown off toner by the use of an electrometer. The cell with the remaining carrier was weighted again to determine the quantity of the toner lost. Figure 2.5 shown the schematic diagram of the tribocharge using the "blow off" method is shown The tribocharge of the toner is calculated based on Equation 2.3 as shown below:

$$Triboch\arg e = -\frac{Ch\arg e\ value\ recorder\ on\ the\ electrometer\ (\mu C)}{mass\ of\ the\ toner\ (g)} \qquad \textbf{[2.3]}$$

2.5.7 Relative Dielectric Constant

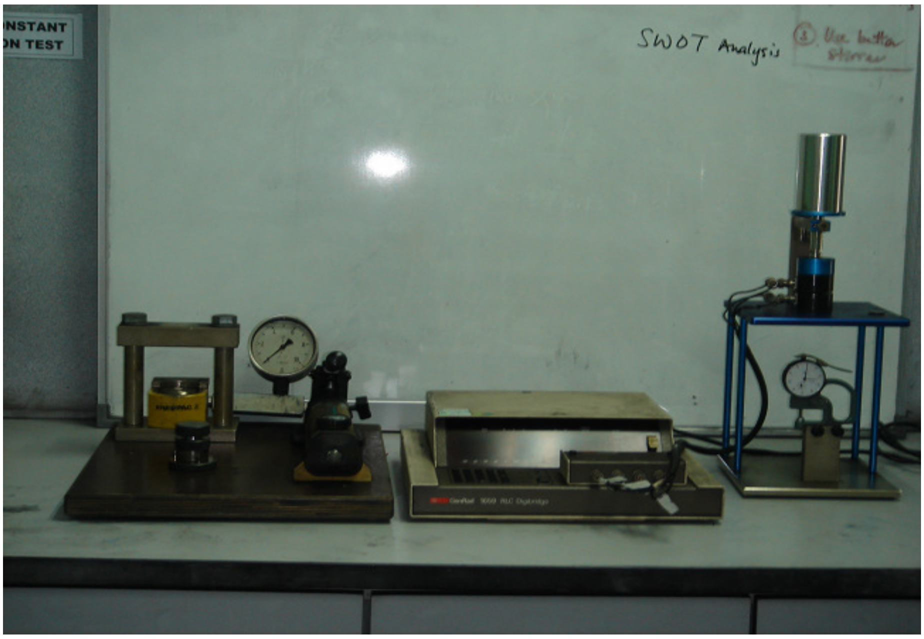

Figure 2.8: Picture of relative dielectric constant instrument

Figure 2.8 is the instrument to measure the relative dielectric constant of the finished toner. The relative dielectric constant of a material under given conditions is a measure of the extent to which it concentrates electrostatic lines of flux. It is the ratio of the amount of stored electrical energy when a potential is applied, relative to the permittivity of a vacuum. The relative static permittivity is the same as the relative permittivity evaluated for a frequency of zero.

The relative static permittivity is represented as ε_r or sometimes κ or K or Dk. It is defined as:

$$\varepsilon_r = \frac{\varepsilon_s}{\varepsilon_o}$$

where ε_s is the static permittivity of the material, and ε_o is vacuum permittivity. (The relative permittivity is the complex frequency-dependent $\frac{\varepsilon(w)}{\varepsilon_o}$, which gives the static relative permittivity for $\omega = 0$.)

Another term for the **relative dielectric constant** is **relative static permittivity** or **static relative permittivity**. By definition, the relative permittivity of vacuum, where $\varepsilon = \varepsilon_0$, is equal to 1. The static relative permittivity of a medium is related to its static electric susceptibility, χ_e by

$$\varepsilon_r = 1 + \chi_e$$

in SI units [58].

In physics, the dissipation factor (DF) is a measure of loss-rate of power of a mechanical mode, such as an oscillation, in a dissipative system. For example, electric power is lost in all dielectric materials, usually in the form of heat. DF is expressed as the ratio of the resistive power loss to the capacitive power, and is equal to the tangent of the loss angle.

The relative dielectric constant dissipation factors were measured accordance with ASTM D2520-95 with some modifications to suit the materials as well as equipment here. The raw toner samples were pressed into a round pellet of thickness in the range of 1.00 to 2.00 mm. The pellet was then put into the sample compartment to get the reading of both the relative dielectric constant and dissipation factor.

2.5.8 Flowability

Figure 2.9: Picture of the flowability instrument

Figure 2.9 is the instrument to measure the flowability of the finished toner. There are not significant differences between the raw toner and after blending finished toner for most of the properties such as molecular weight distribution, particle size distribution, sharpness index, melt flow index, relative dielectric constant, dissipation factor, glass transition temperature, wax melting point and wax content. The only properties that might differ obviously will be the tribocharge as the charge of the toner will be distributed more evenly after additive blending with silicas. Besides, there are two additional properties which are the flowability and apparent density are required to check only at the finish toner stage.

The apparatus consists of a receptable cylinder with interchangeable discs with holes of various diameters; 3, 4, 5, 6, 7, 8, 9, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32 and 34 mm at the bottom. The determination of flowability is based upon the ability of the powder to fall freely through a hole in the disc. The smaller the hole through which the powder falls freely, the better is the flowability of the toner.

The basis for this method is the powder's ability to fall freely through a hole in a plate. The diameter of the smallest hole through which the powder can pass 3 times out of 3 measurements is taken as the flowability index. The ring is secured to the bearing to allow the bottom of the funnel to be near but not touching the powder surface.

Approximately 50.0 g of finished toner powder was poured through the funnel into the middle of the cylinder. When loading was completed, 10 seconds must be allowed for possible formation of individual flocculate or mass flocculation of the whole load. Now the lever device was operated to open the hole in the disk quickly and without vibration.

Flowable toner powder will slowly flow through the small-diameter holes, leaving a cavity shaped like an upside-down, truncated cone. On the other hand, toner powder that flocculates in bulk will fall abruptly, forming a cylindrical cavity. If the experiment is negative, the toner powder must be tested again with a disk having a larger hole that usually graduated sizes differing in 1 to 2 mm. The experiment was repeated 3 times on the hole that the finished toner can flow to confirm the reading. The flowabilty index for most of the CPT finished toners is in the range of 3 to 5 mm^2.

2.5.9 Apparent Density

In use all over the world, the Hall Flowmeter has been covered by ASTM and MPIF Standards since 1945. The apparent density provides a guide for evaluation on the physical characteristic of powders. The density measured bears some relationship to the weight of powder that will fill a fixed volume die cavity when parts are being made.

The apparent density test was done in accordance to ASTM B417-95. The finished toner was loaded carefully into the flowmeter funnel and allowed it to run into the density cup through the discharge orifice. If necessary, the toner may be agitated or pushed by used of a wire but take care to prevent the wire from entering the density cup. The density cup should not be moved during the filling operation.

When the finished toner powders have completely filled and overflowed the periphery of the density cup, rotate the funnel approximately 90° in a horizontal plane so that the remaining powder falls away from the cup. A nonmagnetic spatula was used, with the blade held perpendicular to the top of the cup, leveled off the excess toner powders at the top of the density cup. After leveling operation, the density cup was tapped lightly on the side to settle the powder to avoid spilling in transfer. The density cup with finished toner powders were weighted to the nearest 0.1 g and results shall be reported in g/cm^3 to two places of decimal. The calculation of the apparent density is carried out using the following equation: [59]

$$Apparent\ density,\ g/cm^3 = weight\ in\ gram \times 0.04$$

2.5.10 Microscopic

Picture 2.10: Picture of the microscope

In order to check the fusing of these toner particles, the pictures of these particles were taken using black and white instant 3 ¼ × 4 ¼ in (8.5 × 10.8 cm) Polaroid 667 film and Nikon AFX-DX microscope. Pictures were taken at 40X and 100X magnifications. These pictures are able to tell whether the toner particles can fuse well or not. The pictures also can tell the morphology of these particles for example the shape of these particles whether they are sphere, potatoes or popcorn shapes.

2.6 Latex Blending

The copolymer isolated from latex E149/08 (1.0% CTA) has low MFI but unable to produce raw toner with give good fusing during emulsion-aggregation process. On the other hand, the copolymer isolated from latex of E130/07 (1.4% CTA) has slightly higher MFI but able to produce raw toner with good fusing during emulsion-aggregation process. Hence, to obtain the copolymer of lower MFI and at the same time enable good fusing during EA process, latexes E149/08 and E130/07 were chosen to blend in various ratio to study the effect. The latexes were blended in the ratio of 20:80, 30:70, 40:60, 50:50, 60:40, 70:30 and 80:20. The properties for the latexes were measured and shown in Chapter 3.

2.7 Preparation of raw toner using emulsion-aggregation process using blended latex

The materials and compositions of the reaction mixtures were summarized in Table 2.11. In the emulsion-aggregation process, the latex blended in the ratio 50:50 of latex E149/08 to latex E130/07 was used throughout the experiments because the copolymer isolated from this blended latex properties showed the desired MFI and T_g.

The latex blended in the ratio 50:50 of latex E149/08 to latex E130/07 of total solid content of 38.25%, aqueous Clariant pigment dispersion (Carbon Black, Yellow, Cyan or Magenta) of dry solid contents of 20.0% and N24 (proprietary formulation), charge control agent (CCA) were simultaneously added to the distilled water with high shear stirring by means of IKA Ultra-Turrax T25 Basic Homogenizer for 5 minutes. After that, the O-307 wax dispersion with dry solid contents of 35.0% was added into the mixture with continuous high shear stirring for another 5 minutes. To this mixture, 1.60 g polyaluminium chloride (PAC) was added over a period of 3 minutes with continuous homogenizing at speed of 9500 rpm for a period of 5 minutes. The pH of the resulting mixture was adjusted to 3 before it was transferred to a 1L reactor flask and heated to 57°C. The aggregation process was carried out for 4 hours. The pH of the mixture was then adjusted from pH 2.2 to pH 8.0 with a base solution of 4% sodium hydroxide. Subsequently, the mixture was heated from 57°C to 95°C and the pH of the mixture was adjusted back from pH 7.2 to pH 6 using 0.2 M nitric acid. The coalescences process was retained for a period of 3 hours before cooling down to room temperature.

Table 2.11: Materials used for EA process on latex ratio 50:50

Ingredients	Solid content (%)	% of dried weight	Amount Used (g)
Resin	38.25	85	137.25
Pigment Dispersion	20.00	5	15.00
Wax Dispersion	35.00	8	13.70
CCA	60.00	2	2.00
Commercial PAC		-	1.60
Distilled Water		-	280.35

2.8 Isolating, washing and filtering the raw toner

The wet cake raw toner has to undergo washing and isolated by filtration followed by drying before additive blending. The normal washing using distilled water up to four times was not sufficient to remove all the impurities and the excess raw materials that were not used during the reactions. Thus, this wet cake raw toners were washed and isolated by filtration for four times with different conditions before drying. Firstly, the wet cake was stirred at 300 rpm for an hour in alkaline condition (pH 11) and isolated by filtration; followed by two times stirring at 300 rpm for an hour in distilled water and isolated by filtration. Finally, the wet cake raw toners were stirred at 300rpm for an hour in acidic condition (pH 4) and isolated by filtration. Lastly, the wet cake raw toners were dried in vacuum oven at 40°C for 48 hours until all the moisture was fully removed.

2.9 Additive Blending

Additive blending of raw toner is basically a process to allow the external additives mainly like silica to improve certain properties of the toner. The silicas are divided into different size to improve on different properties. The sol-gel type also known as the large size silica helps on the cleaning ability and control the transfer efficiency. The medium size type like hydrophobic fumed silica helps to reduce adhesion forces and improve the transfer efficiency of the toner whereas the small hydrophobic fumed silica acts as a powder flow promoter. Besides silica, other additives like zinc stearate can help to prolong the photoconductor life.

Two different blending had carried out using two types of silica; small and big silica which were SS50F and RY200L2 (proprietary formulation). After the final blending, the finished toner was used in test print and performance test. The results will be shown in Chapter 3. Table 2.12 below showed the formulation used in the additive blending.

Table 2.12: Formulation used in additive blending

Sample	**Raw Materials Used (g)**				
	Raw Toner (g)	**SS50F**		**RY200L2**	
		Percentage (%) of the raw toner	**Weight (g)**	**Percentage (%) of the raw toner**	**Weight (g)**
KFT01/08	150.0	1	1.5	2	3.0
KFT06/08	150.0	1	1.5	2	3.0

Although both the blending cases used the same amount of additives and raw toner but both cases were blended in the different method. As for case KFT01/08, the raw toner and 1% SS50F were blended at 4244 rpm for 3 minutes followed by the addition of 2% RY200L2 blended at 4244rpm for another 3 minutes. As for case of KFT06/08, the raw toner and 1% SS50F were blended at 5000rpm for 3 minutes continuously for 2 times, followed by the addition to 2% RY200L2 blended at 4244 rpm for 2 minutes. Then, the mixture was allowed to stop blending for 2 minutes before proceeding to another blending of 4244 rpm for 2 minutes. The finished toners were used to performance test print and performance test.