CHAPTER 4

RESULTS AND DISCUSSION

4.1 Effect of the Pigment/Binder Ratio on the Pigmented Inkjet Ink Properties

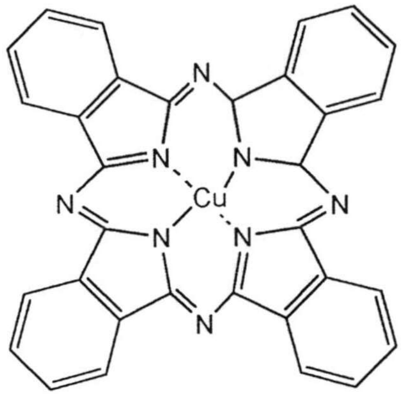
The effect of pigment/binder ratio in an ink formulation on ink properties was evaluated. Based on these four different pigment dispersion technologies, polymer dispersion, surfactant dispersion, micro-encapsulation, and surface modification, polymer dispersion is to stabilize a water insoluble pigment with a water-based polymer,(8) while stabilization of surfactant dispersion is generated after adsorption of a thin layer of surfactant onto the pigment surface.(10) Micro-encapsulated pigments have the thick acrylic polymers with self-dispersibility on the pigment surfaces,(11) and the last one, surface modification of the pigment by attaching sulfonic groups imparts desirable physicochemical properties of the system.(12)

4.1.1 The Properties of Pigmented Inkjet Ink

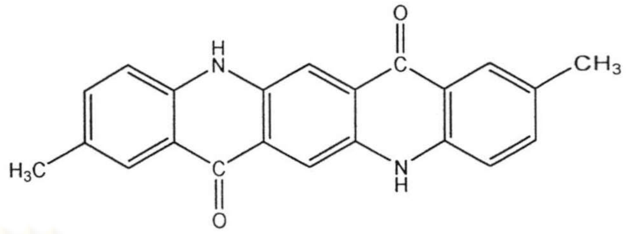
The properties of four types of pigment dispersion techniques are shown in Table 3-1.

The chemical class of pigments as shown in Figure 4-1, phthalocyanine pigments are the standard bright greenish blue shades. Transparency, brightness, tinting strength, color purity and high degree of permanency are characteristics of the phthalocyanine pigment class. Pigment Blue 15:4 is an ideal chroma for process color printing. Solvent and heat stable, greener, less bronzing tendency of PBl 15:4 (beta crystal form) are weaker than alpha crystal forms (PBl 15:3).(35) Pigment red 122 is a bright bluish-shade red with high performance and high degree of intermolecular bonding.(35) Yellow shade can be composed using Pigment yellow 74, 128 and 138. Pigment yellow 74 has a bright yellow shade with superior brightness.(44) Pigment yellow 128 and 138 are greenish-shade yellow. Pigment Black 7 is the most important black pigment, which is composed of 90-99% carbon.(35)

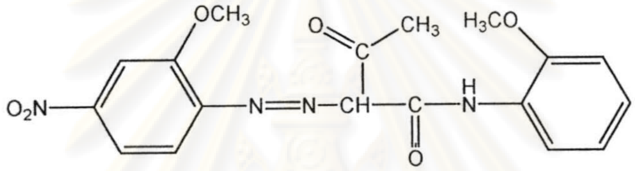
The pigments are dispersed well below 1 micrometer level. Median diameters of the dispersions were in the range of 100-200 nm. Surface modification technique gave blue and red pigment dispersion with a smaller median diameter than others. The pigment dispersed by surfactant dispersion and polymer dispersion techniques showed a smaller median diameter of yellow and carbon black. Characteristic features of pigment dispersion are low viscosity, stable at high pH (>7). Surface modification technique gave the dispersed pigments with a high pH and viscosity. The surface modified pigments with sulfonate groups are stable over a wide pH range (3-10). The physical property data for four sets of color pigments produced by various pigment dispersion techniques, are appropriate for inkjet water-based applications.



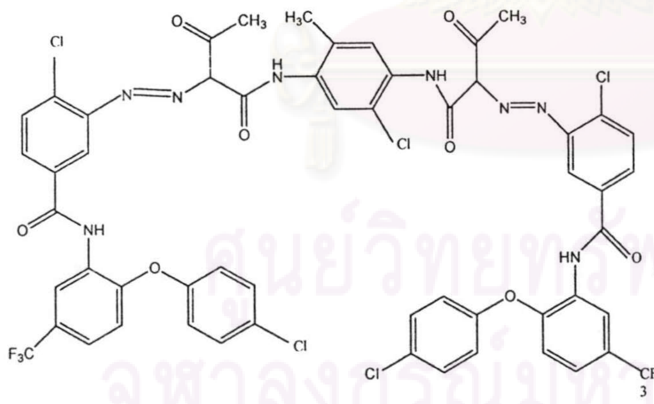
C.I. Pigment Blue 15:3 (35)



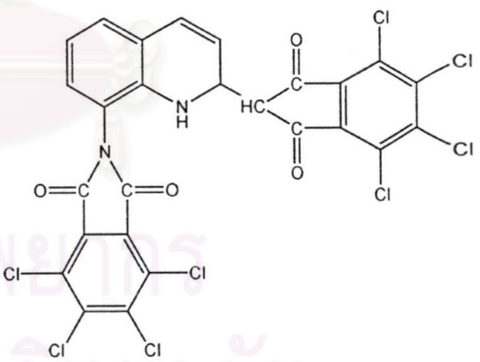
C.I. Pigment Red 122 (35)



C.I. Pigment Yellow 74 (44)



C.I. Pigment Yellow 128 (35)



C.I. Pigment Yellow 138 (35)

Figure 4-1 Chemical structures of pigments

Four sets of pigmented inkjets inks with various pigment-to-binder ratios (1/0.5, 1/1, 1/2) were prepared. Therefore the tinting strength is high, the concentration of pigment in the ink can be, or should be decreased to below 6%. The tinting or coloring strength increases with decreasing the particle size. The properties of organic solvent in the ink formulation depend on the nature of the dispersed pigment particles. Generally the solvent concentration is of around 10% to 15%. Many types of the organic solvents at different concentrations are used. The additive, usually a surfactant, which concentrations are from 0.1% to 1.5%. There is some special cases where the surfactant concentration is 1.5% or more. In such a case, the surfactants were not used to tune the surface tension, but were used as solvents for the special dyestuffs, which have a lower solubility in water. The surfactant always gives rise to foaming of an ink. The addition of approximately 2.5% urea to the ink formulation was found to significantly reduce the clogging problem of a printhead. This additive also improved the jetting characteristics of the ink. No other additives were used in the ink formulation. Table 4-1 shows the properties of pigmented inkjet inks, the ink formulations of each pigment dispersion are differed by varying the pigment/binder ratios as 1/0.5, 1/1 and 1/2. The inks with a pigment loading of 3.5% and binder contents of 1.75%, 3.5% and 7% could be successfully jetted. Through the pH, viscosity and surface tension of the pigmented inkjet inks presented in Table 4-1.

Table 4-1 The properties of pigmented inkjet inks

Pigmented inkjet inks	Polymer dispersion			Surfactant dispersion			Micro-encapsulation			Surface modification		
	viscosity (mPa s)	Surface tension (mN/m)	pH	viscosity (mPa s)	Surface tension (mN/m)	pH	viscosity (mPa s)	Surface tension (mN/m)	pH	viscosity (mPa s)	Surface tension (mN/m)	pH
1/0.5*												
Cyan	2	45.6	8.3	2.1	47.2	8.5	2	39.3	8.8	1.7	51.2	8.3
Magenta	2.4	46.2	8.3	2.2	50.5	8.4	2.1	40.9	8.8	1.8	53.7	8.3
Yellow	2.1	45.7	8.3	2.1	45.5	8.3	2.5	43.1	8.9	1.8	50.4	8.2
Black	2.2	46.4	8.4	2.3	47.6	8.3	3	39.4	8.9	1.8	43.2	8.5
1/1.0*												
Cyan	2.4	45.7	8.4	2.1	46.1	8.3	2.3	40.3	8.7	2	50.9	8.3
Magenta	2.5	49.5	8.7	2.2	45.4	8.4	2.5	40.5	8.6	2	53.6	8.7
Yellow	2.4	48.7	8.4	2.2	45.1	8.3	3.1	42.7	8.8	1.9	50.3	8.3
Black	2.3	47.3	8.5	2.5	47.8	8.3	3.2	38.7	8.7	1.9	45.8	8.3
1/2.0*												
Cyan	2.8	45.9	8.3	2.6	43.3	8.3	2.9	40.6	8.4	2.2	49.9	8.3
Magenta	2.9	43.2	8.3	2.7	46.7	8.3	3.1	40.3	8.3	2.3	53.3	8.4
Yellow	2.7	47.8	8.4	2.7	46.4	8.3	4.5	42.1	8.4	2.2	53.3	8.4
Black	2.9	46.7	8.3	3.2	47.0	8.4	4.4	38.6	8.4	2.5	44.5	8.2

* = Pigment/Binder ratio

The properties namely viscosity and surface tension of ink used for the inkjet printing are quite different from those used in the traditional textile printing system. Various inkjet inks are characterized in terms of pH, surface tension and viscosity, as these properties have a significant impact on the printing quality through a droplet formation, ink spreading and penetration.

4.1.1.1 Effect of P/B Ratio on Surface tension of the Pigmented Inkjet Inks

Surface tension helps regulate control of the concave meniscus to hold ink in the system. Once the ink has been deposited onto the printing substrate, the interaction of the surface dynamics of both the ink and substrate plays a major role in how the final form of the dot will appear. It is apparent that an increase in the binder concentration has little effect on surface tension as shown in Figure 4-2. Surface tension data of all pigmented inkjet inks prepared by various pigment/binder ratios are not affected by the amount of binder used.

Surface tension of pigmented inkjet inks made from surface modified pigment gave inks with high surface tension. Characteristic features of these techniques are of high surface tension (>70 dynes/cm).(12)

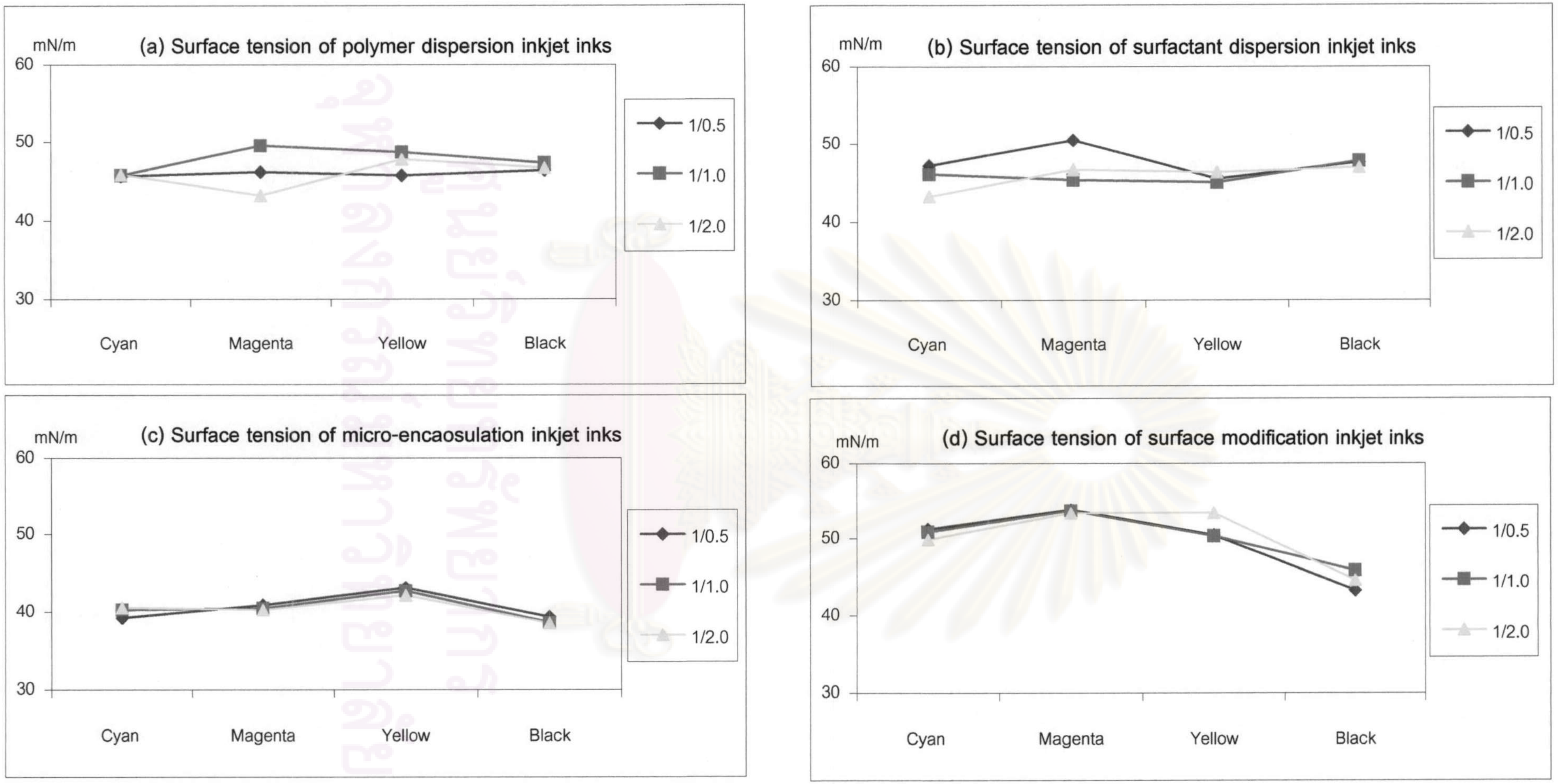


Figure 4-2 Effect of pigment/binder ratio on surface tensions of the pigmented inkjet inks prepared by different dispersion technologies: (a) Polymer dispersion, (b) Surfactant dispersion, (c) Micro-encapsulation and (d) Surface modification.

4.1.1.2 Effect of P/B Ratio on Viscosity of the Pigmented Inkjet Inks

The increasing binder content increases the viscosity as shown in Figure 4-3. From the viscosity analysis of all the pigmented inkjet inks prepared by the polymer dispersion, surfactant dispersion, micro-encapsulation and surface modification, it was found that the 3.5% pigment, and 7% binder formulation gave the higher viscosity than those of all types of pigment dispersion techniques.

The viscosity of inkjet inks depends on the amount of polymer in ink and viscosity of dispersed pigment. The dispersed pigment with high viscosity also gave high viscosity ink. As shown in Table 4-1, the highest viscosity of pigments dispersed by polymer dispersion, surfactant dispersion, micro-encapsulation and surface modification are magenta, black, yellow, and black pigments, respectively. Figure 4-3 shows the pigments with high viscosity value also gave the high viscosity ink.

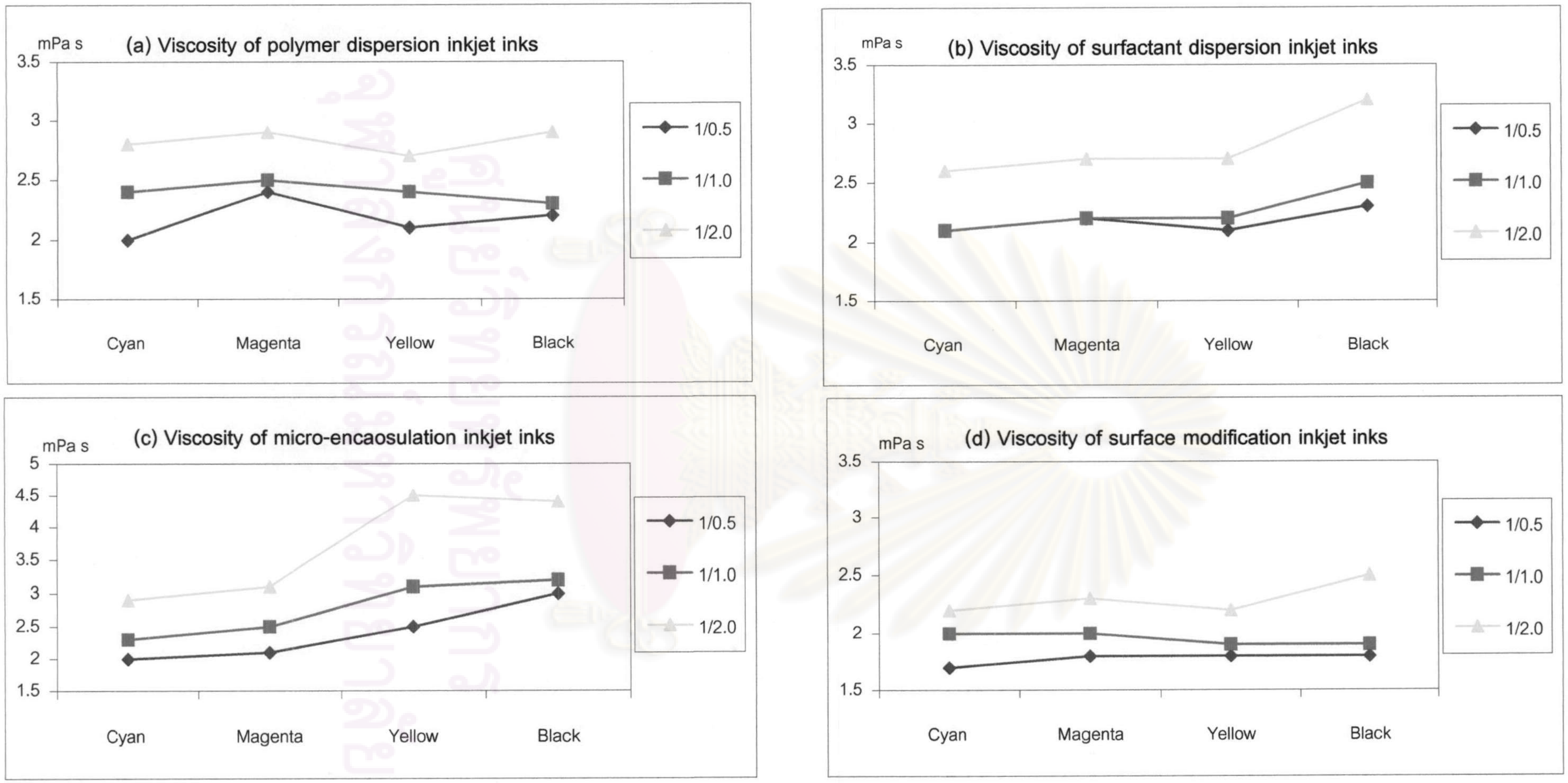


Figure 4-3 Effect of pigment/binder ratio on viscosity of the pigmented inkjet inks prepared by different dispersion technologies: (a) Polymer dispersion, (b) Surfactant dispersion, (c) Micro-encapsulation and (d) Surface modification.

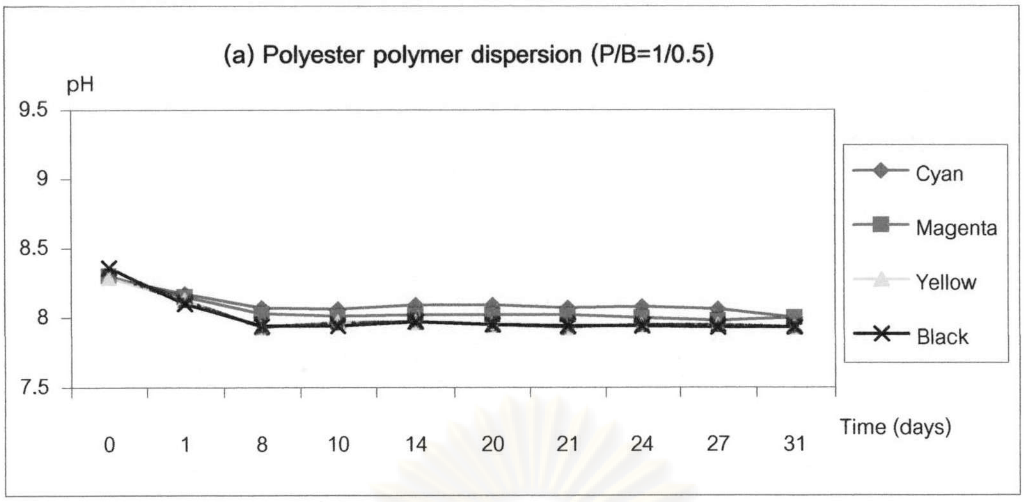
4.1.2 The Stability of the Pigmented Inkjet Ink

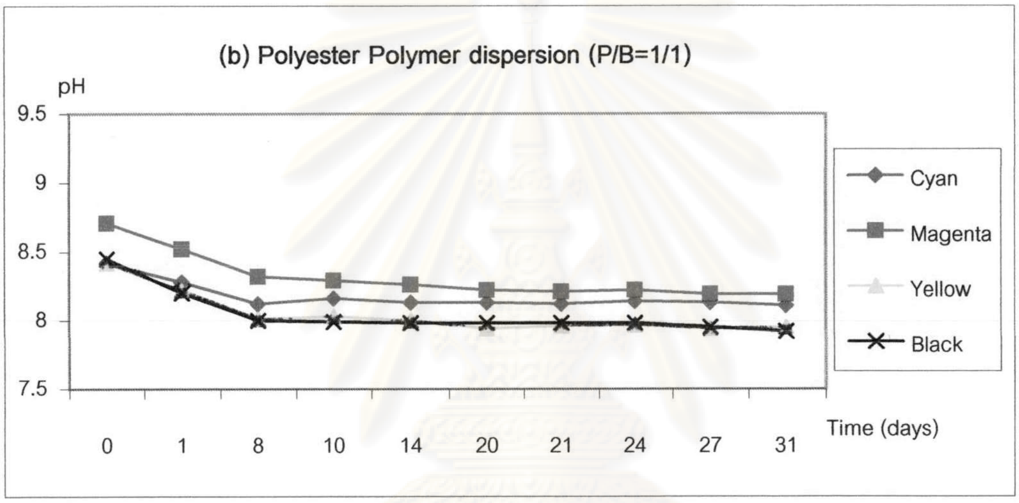
4.1.2.1 Effect of P/B Ratio on pH Stability

The pH of the inkjet ink is critical for several reasons. The hue of some colorants will change if they go from a low to high pH value. There must be a correlation between the pH values of the ink and of the printing media; otherwise, the archival quality of the print may be deteriorated. Another reason for controlling pH of the ink is that the orifice of some inkjet system may be made of a material that is affected by pH. In other words, the orifice diameter or dimension may be changed because the solution pH affects its shape stability.

Figures 4-4 to 4-7 show the pH stability of various pigmented inkjet inks after being stored at room temperature for 2 months. To mention again, the pigmented inkjet inks were prepared by the various dispersion technologies at the pigment/binder ratios of 1/0.5, 1/1 and 1/2.

After two months of storage, the properties of the pigmented inkjet inks were unchanged. The effect of pigment/binder ratio on pH stability of all the pigmented inkjet inks gave the acceptable results because the pH values after 60 days storage is still in the control range (7-10).


(a) Polyester polymer dispersion (P/B=1/0.5)


(b) Polyester Polymer dispersion (P/B=1/1)

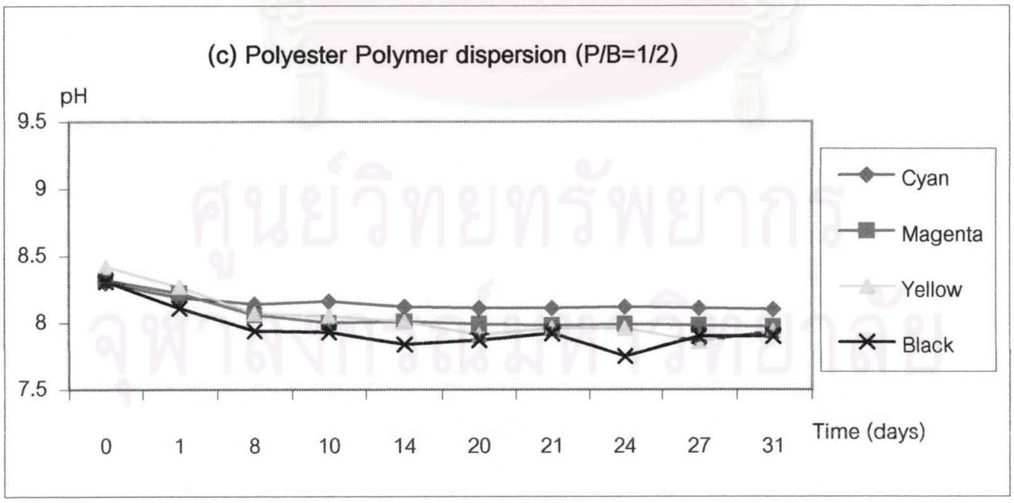
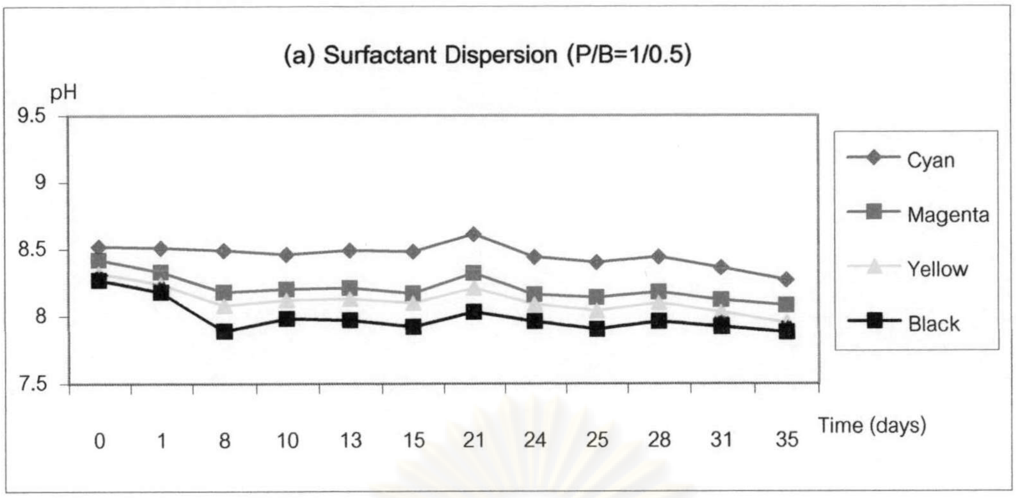
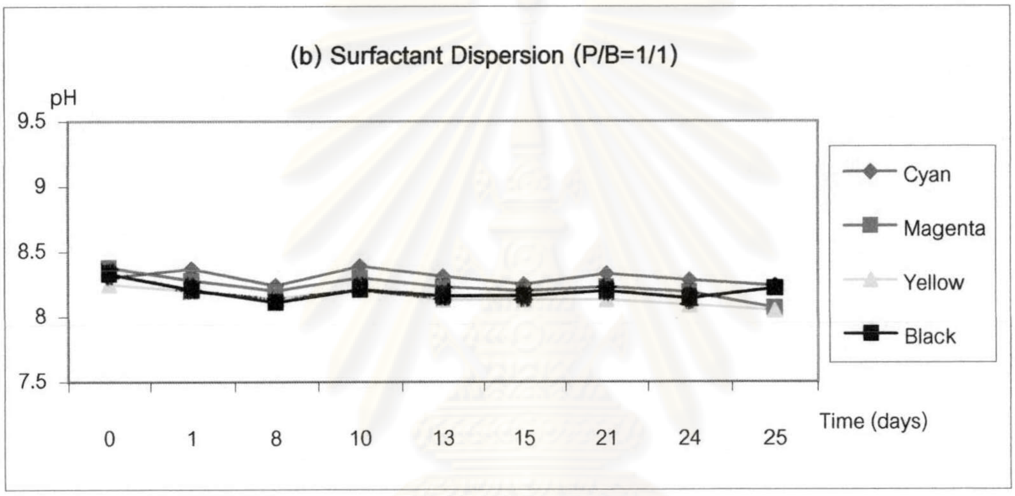

(c) Polyester Polymer dispersion (P/B=1/2)

Figure 4-4 The pH stability of pigmented inkjet inks made from polymer dispersion with various P/B ratios: (a) 1/0.5, (b) 1/1 and (c)1/2


(a) Surfactant Dispersion (P/B=1/0.5)


(b) Surfactant Dispersion (P/B=1/1)

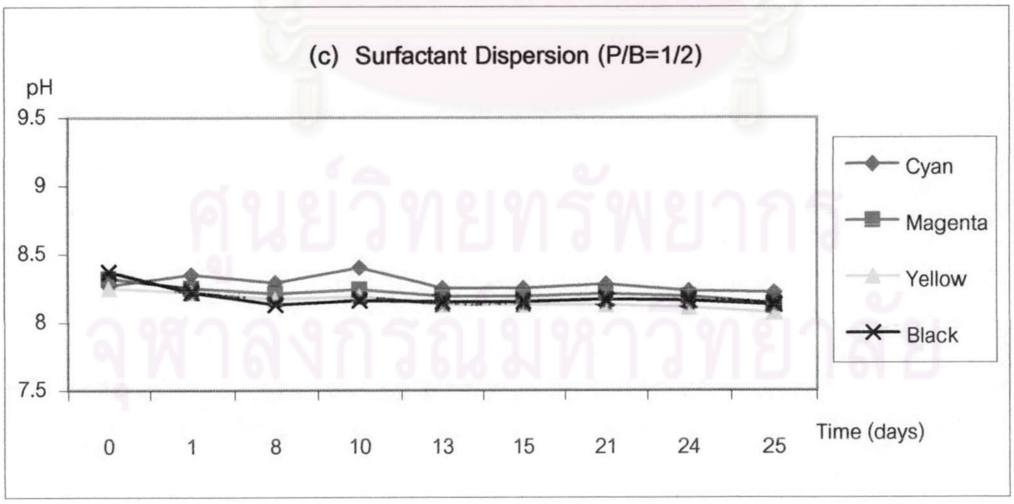
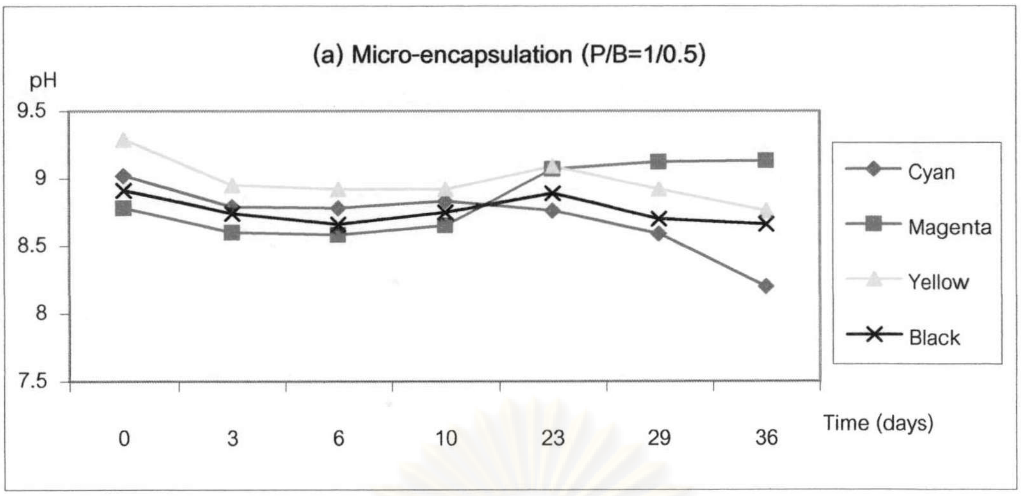
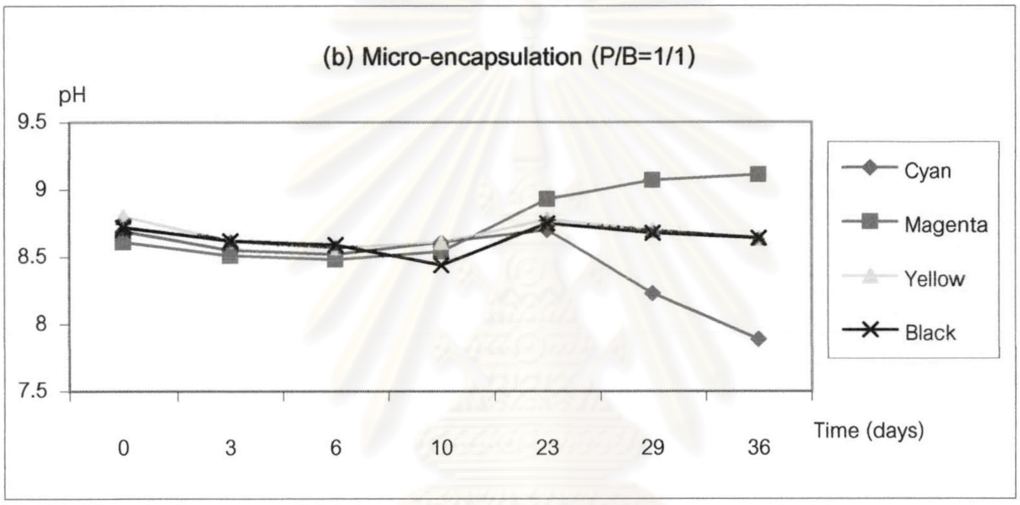

(c) Surfactant Dispersion (P/B=1/2)

Figure 4-5 The pH stability of pigmented inkjet inks made from surfactant dispersion with various P/B ratios: (a) 1/0.5, (b) 1/1 and (c)1/2





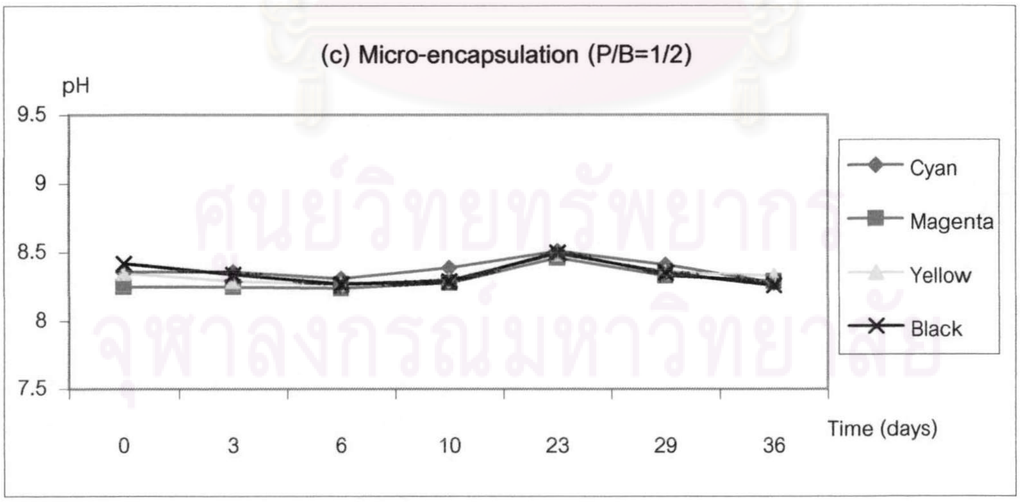
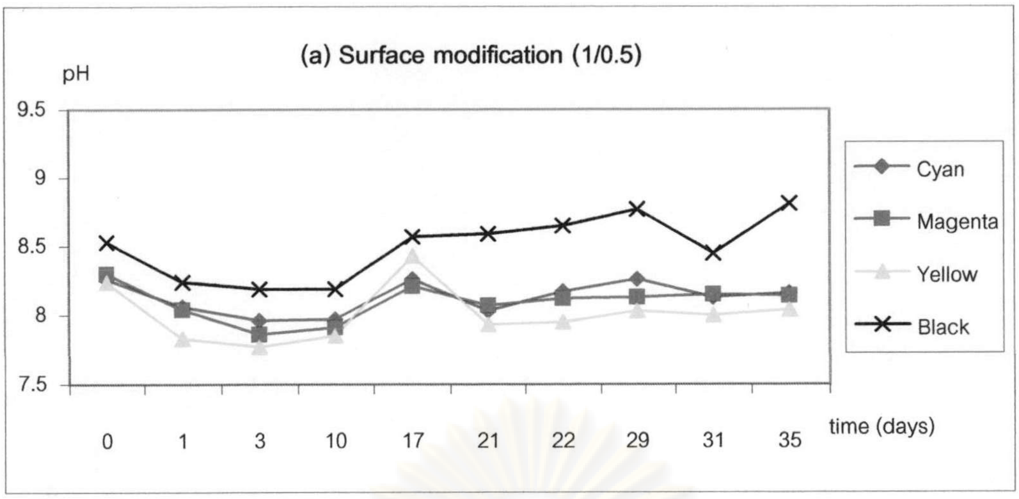
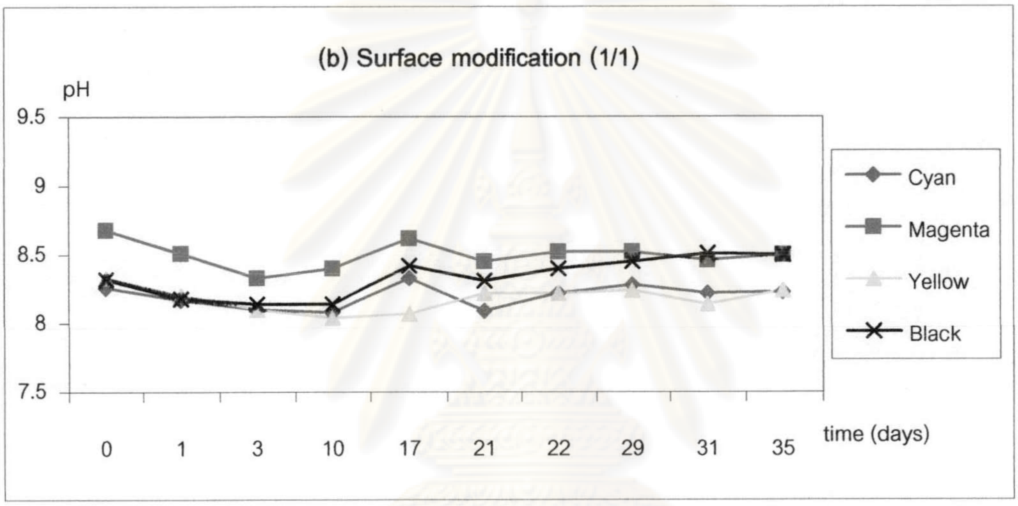


Figure 4-6 The pH stability of pigmented inkjet inks made from Micro-encapsulation with various P/B ratios: (a) 1/0.5, (b) 1/1 and (c)1/2





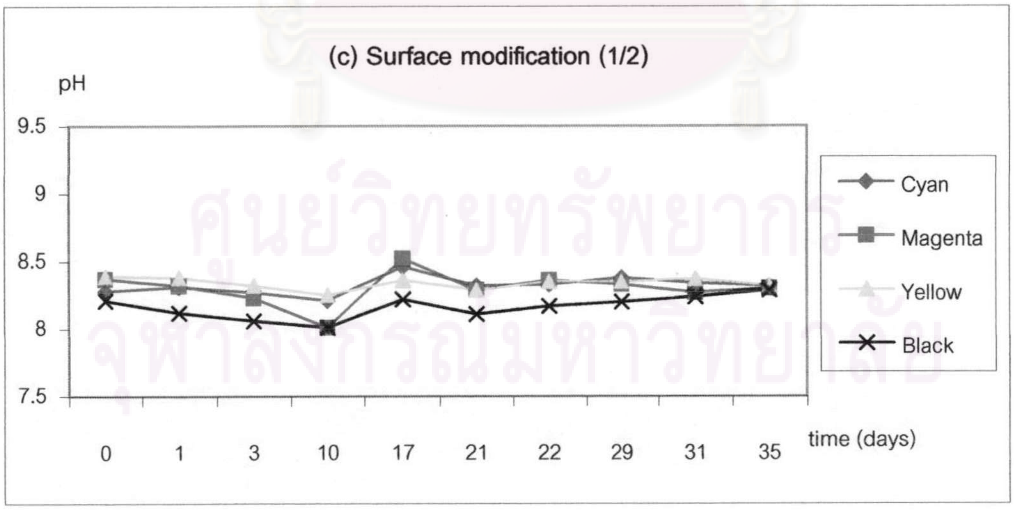


Figure 4-7 The pH stability of pigmented inkjet inks made from surface modification with various P/B ratios: (a) 1/0.5, (b) 1/1 and (c)1/2

Considering ink properties of inkjet inks prepared from surface modification of the pigment in Figure 4-7, pH at all P/B ratios increased. The pH controlling materials are very small particles, so they can be absorbed into the small pores of the surface modified pigments. The pH values (8-9) are basic.

The pigment particles reach a stable state by an absorption on its surface of the dispersing agent. Stabilization of the dissociated state can be achieved by controling the added salt, ions, impurities in and from outside. These factors affect the size of the hydrostatic, and electrostatic radii of the particles in the vehicle. The polymer dispersion, surfactant dispersion and micro-encapsulation techniques containing color pigments with the carboxylate group (COOH), but surface modification constitutes pigments with sulfonic acid (SO_3H) modified surfaces. The carboxylic moiety shows improved stability in a range of 7-10 over the sulfonic group.

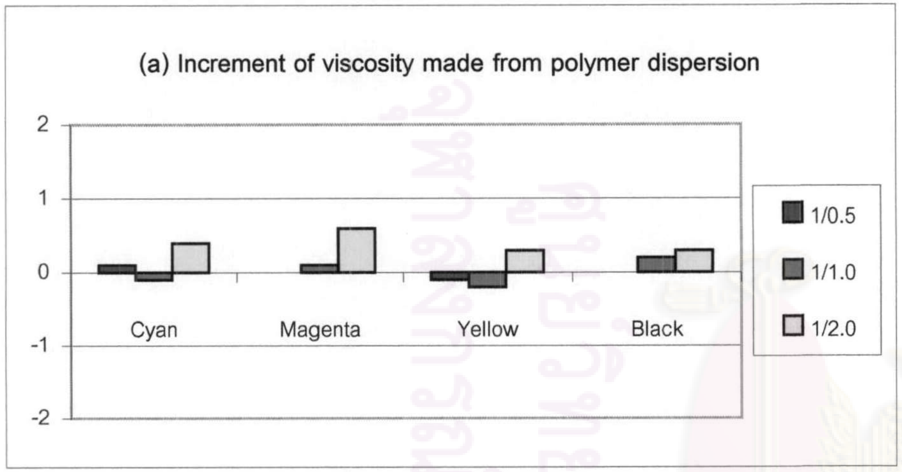
4.1.2.2 Effect of P/B Ratio on Viscosity Stability

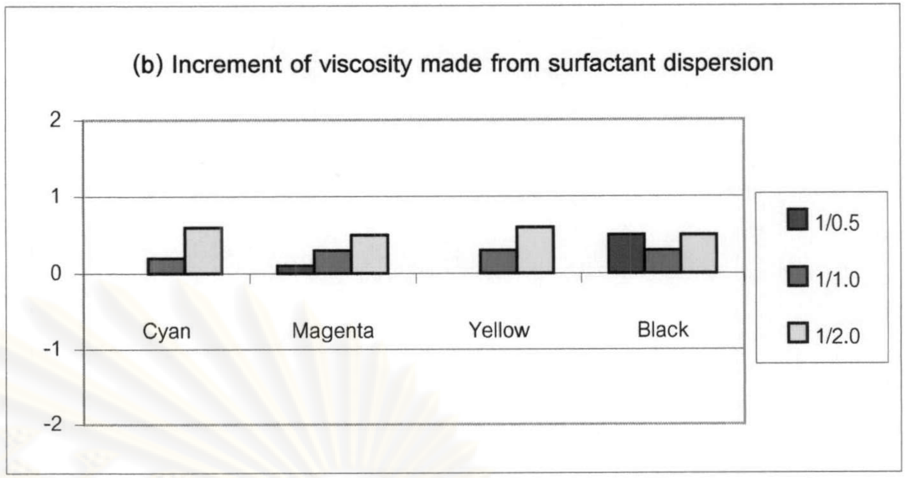
The pigmented inkjet inks prepared by the various dispersion technologies at various pigment/binder ratios were confirmed to be stable after more than two-month storage in the ambient condition. The changes of viscosity after the storage were summarized in Table 4-2.

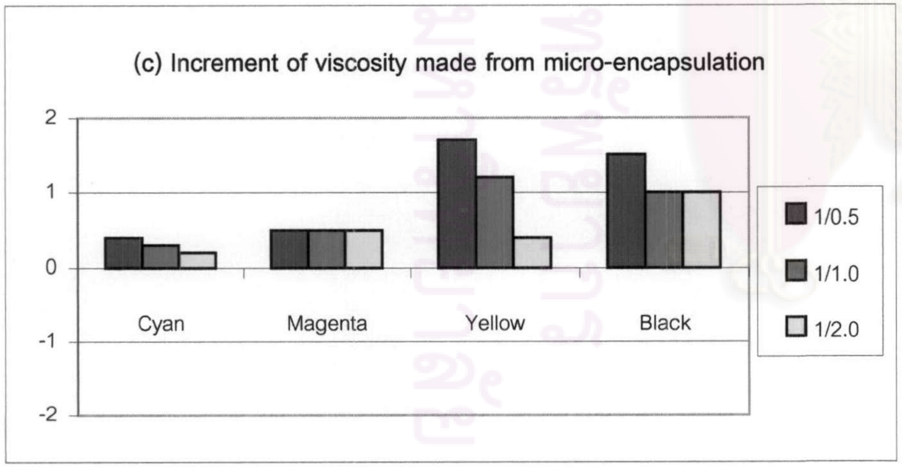
Table 4-2 The changes of viscosity after 60-day storage at room temperature

Pigmented Inkjet inks	Viscosity (mPa s) at 25 °C, spindle # 31					
	1/0.5*		1/1*		1/2*	
	Freshly prepared	After 60-day storage	Freshly prepared	After 60-day storage	Freshly prepared	After 60-day Storage
Polymer dispersion of Cyan	2	2.1	2.4	2.3	2.8	3.2
Magenta	2.4	2.4	2.5	2.6	2.9	3.5
Yellow	2.1	2	2.4	2.2	2.7	3
Black	2.2	2.2	2.3	2.5	2.9	3.1
Surfactant dispersion of Cyan	2.1	2.1	2.1	2.3	2.6	3.2
Magenta	2.2	2.3	2.2	2.5	2.7	3.2
Yellow	2.1	2.1	2.2	2.5	2.7	3.3
Black	2.3	2.8	2.5	2.8	3.2	3.9
Micro-encapsulation of Cyan	2	2.4	2.3	2.6	2.9	3.1
Magenta	2.1	2.6	2.5	3	3.1	3.6
Yellow	2.5	4.2	3.1	4.3	4.5	4.1
Black	3	4.5	3.2	4.2	4.4	5.4
Surface modification of Cyan	1.7	1.9	2	2	2.2	2.6
Magenta	1.8	2.1	2	2.3	2.3	3.1
Yellow	1.8	1.8	1.9	2.1	2.2	2.7
Black	1.8	1.9	1.9	2.3	2.5	3.1

* = Pigment/Binder ratio


(a) Increment of viscosity made from polymer dispersion


(b) Increment of viscosity made from surfactant dispersion


(c) Increment of viscosity made from micro-encapsulation

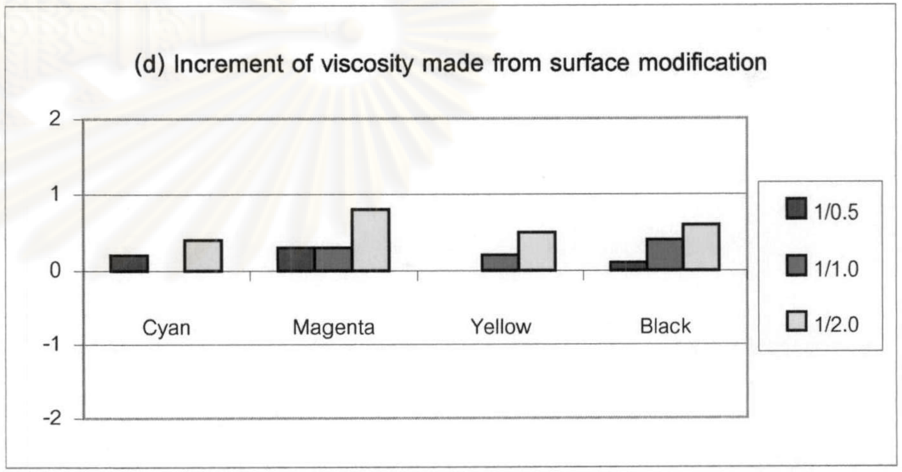
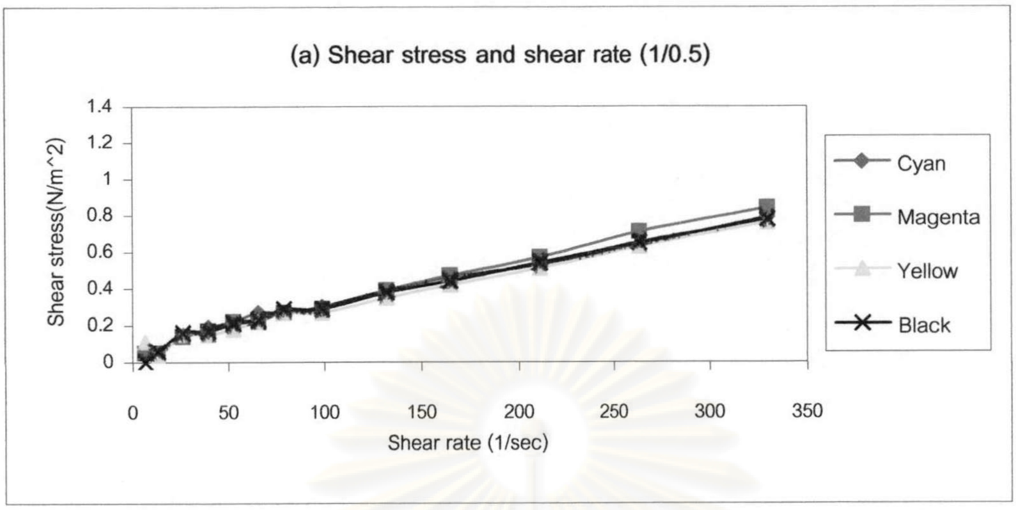
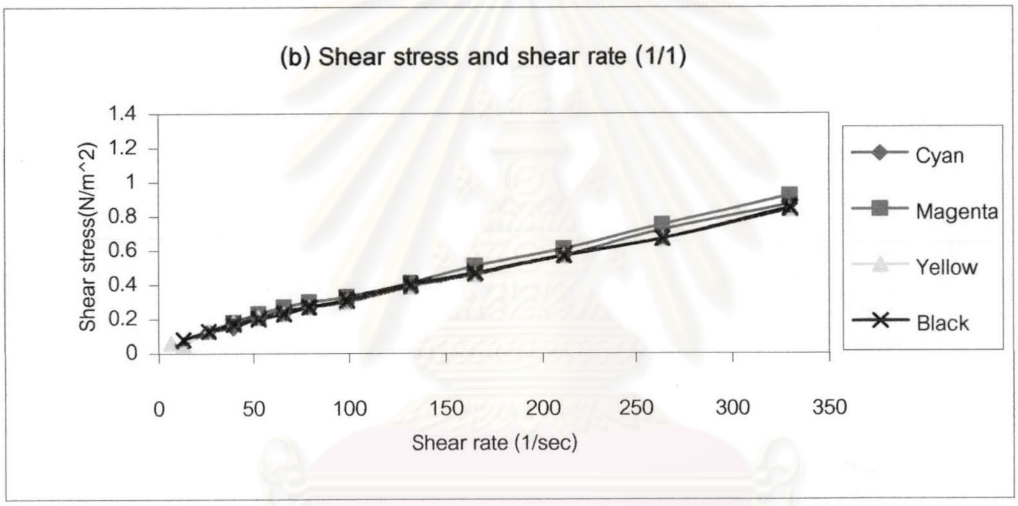

(d) Increment of viscosity made from surface modification

Figure 4-8 Increment of viscosity value at P/B ratio with different pigment dispersion technologies: (a) Polymer dispersion, (b) Surfactant dispersion, (c) Micro-encapsulation, and (d) Surface modification

Table 4-2 and Figure 4-8 show a comparison of viscosity of all pigmented inkjet inks by various pigment/binder ratios. The 1/2 P/B ratio ink has a greater effect than the other ratios in raising the viscosity after about two months of storage under ambient condition. It was found that binder's viscosity increase in ink formulation has an inhibitory effect on stability of viscosity. The viscosity of inkjet inks formulated with polymer dispersion, surfactant dispersion and surface modification technologies at all P/B ratios was stable. On the other hand, the yellow and black inks with micro-encapsulated pigment was inferior in stability since the higher viscosity of inks were found. As the encapsulation polymers are multifunctional, they may work as a flocculant in low pigment/binder ratio regions when all the polymers were supposed to be uniformly adsorbed on pigment particles. Considering the adsorption equilibrium, the quantity of polymer at 1/0.5 and 1/1 ratios may not be sufficient to cover the surface of pigment particle completely. Consequently, increasing binder content exhibits a slightly higher viscosity. In theory, one could increase the viscosity to increase particle size. A general conclusion from Table 4-2 is that the pigmented inkjet inks require stabilizing additives to effectively stabilize the ink viscosity, in this study there are no other additives were used in the formulations for ink stability.

The observed flow behavior of all pigmented inkjet inks is Newtonian in nature. Figures 4-9 and 4-10 represent the rheological behavior of the polymer dispersion pigmented inkjet ink as prepared and after two-month storage . This indicates that the inkjet ink systems maintain a constant viscosity regardless of the type and shear rate.





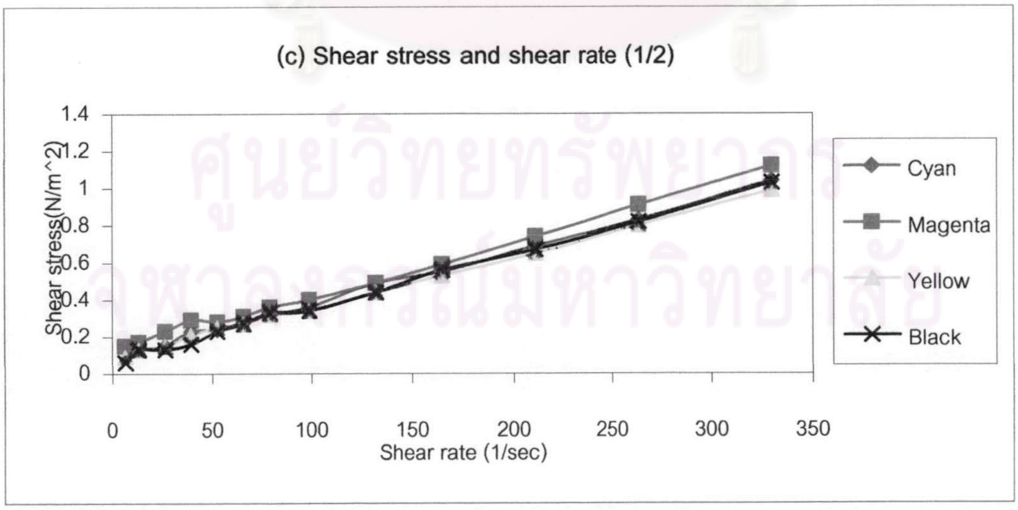
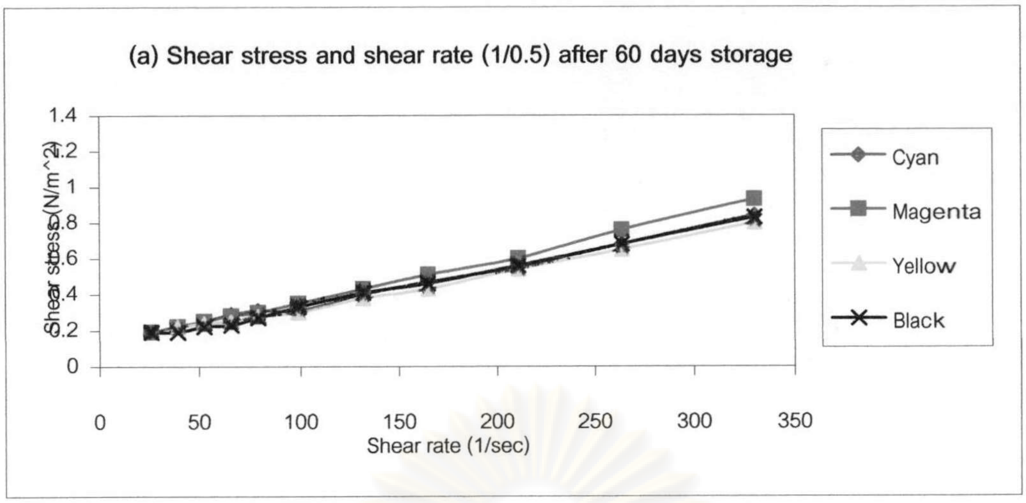
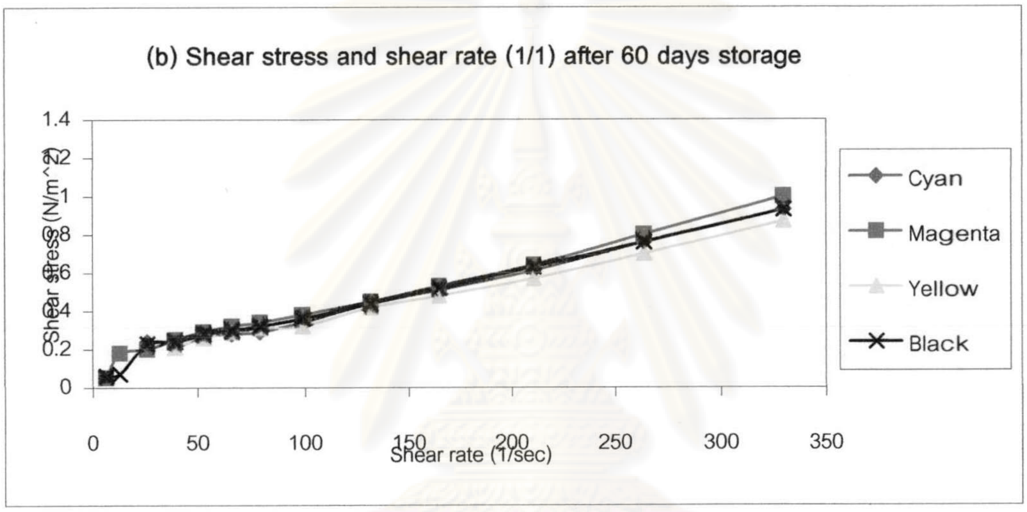


Figure 4-9 Shear stress and shear rate of the pigmented inkjet inks made from polymer dispersion (with various P/B ratios: (a) 1/0.5, (b) 1/1 and (c) 1/2). All are measured right after preparation.


(a) Shear stress and shear rate (1/0.5) after 60 days storage


(b) Shear stress and shear rate (1/1) after 60 days storage

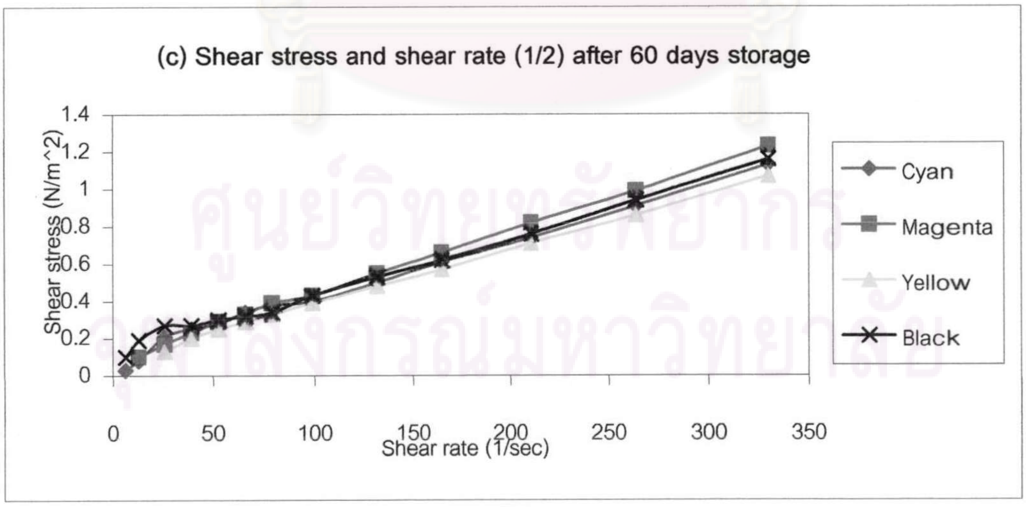

(c) Shear stress and shear rate (1/2) after 60 days storage

Figure 4-10 Shear stress vs shear rate of the pigmented inkjet inks made from polymer dispersion (with various P/B ratios: (a) 1/0.5, (b) 1/1 and (c) 1/2) after 60-day storage at ambient temperature

4.2 Effect of the Pigment/Binder Ratio on the Print Evaluation

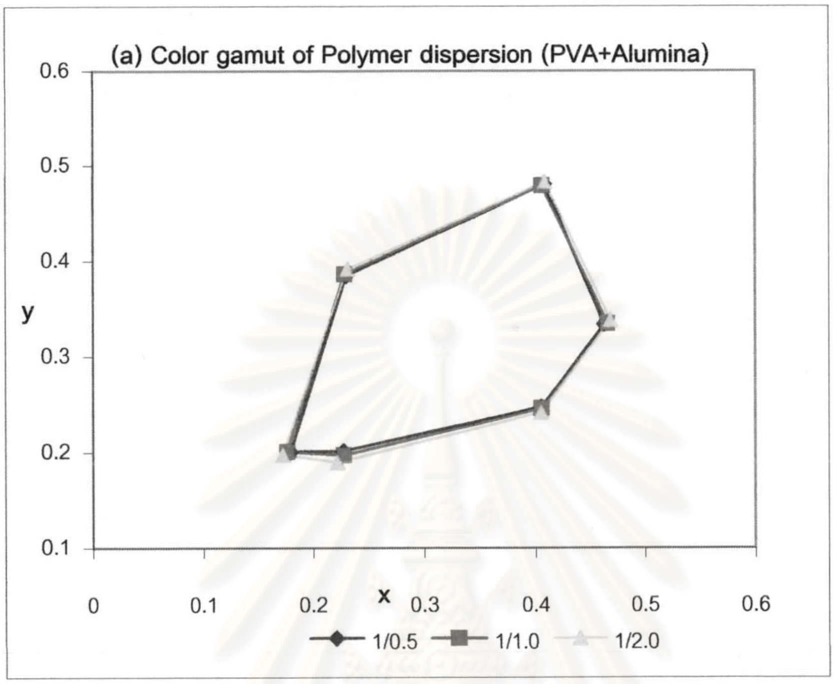
One type of cotton fabric was used to study the effect of the pigment/binder ratio on printed fabrics. Cotton fabrics were pre-treated by the mixed solution of poly(vinyl alcohol) and alumina. The pigmented inkjet inks were printed on the pre-treated cotton fabrics using an Epson inkjet printer (Epson Stylus Color 3000). The printed samples were thermally cured (150°C, 10 minutes) and were tested with no-wet post processing. The printed substrates are evaluated for four properties: color appearance (Gamut and Volume), air permeability, stiffness and wet & dry crockfastness.

4.2.1 Color Gamut and Color Gamut Volume

For the proceeding measurements of color gamut, a standard color space in Figure 3.1 is used to observer the extent of color gamut from the experiments. The color gamut ideally should fix within the xy color space.

The effect of pigment/binder ratio on color behavior of the printed fabrics were evaluated. The color gamut is usually presented in a CIE x-y chromaticity diagram.

It is well known that dye-based inkjet ink has a large color space, high brightness and high transparency, while the pigmented inkjet ink has disadvantages in these properties. To overcome these short coming, a pigmented dispersion has been developed for next generation inkjet ink, from which a significant improvement can be achieved from the existing inks. As mentioned before, all pigmented inkjet inks with 1/2 P/B ratio yielded a smaller color space on the printed fabric as shown in Figure 4-11.



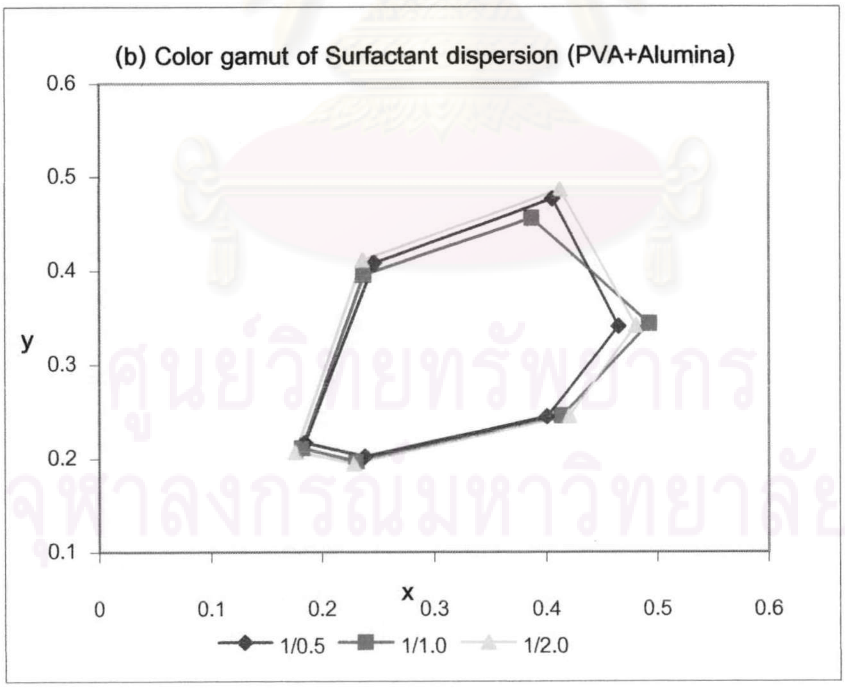
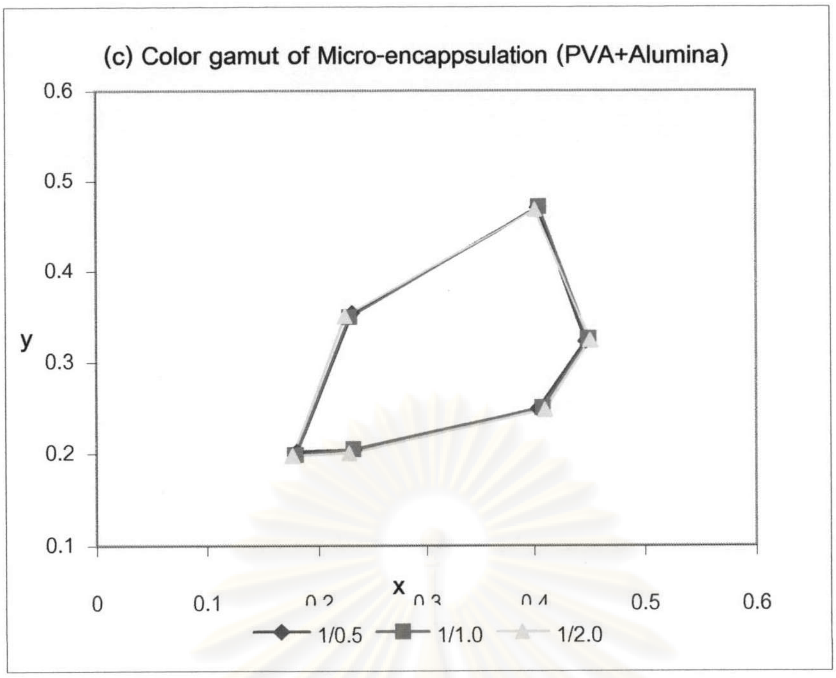


Figure 4-11 Color gamut of the pigmented inkjet inks at different P/B ratios prepared by different dispersion technologies: (a) Polymer dispersion, (b) Surfactnt dispersion, (c) Micro-encapsulation and (d) Surface modification



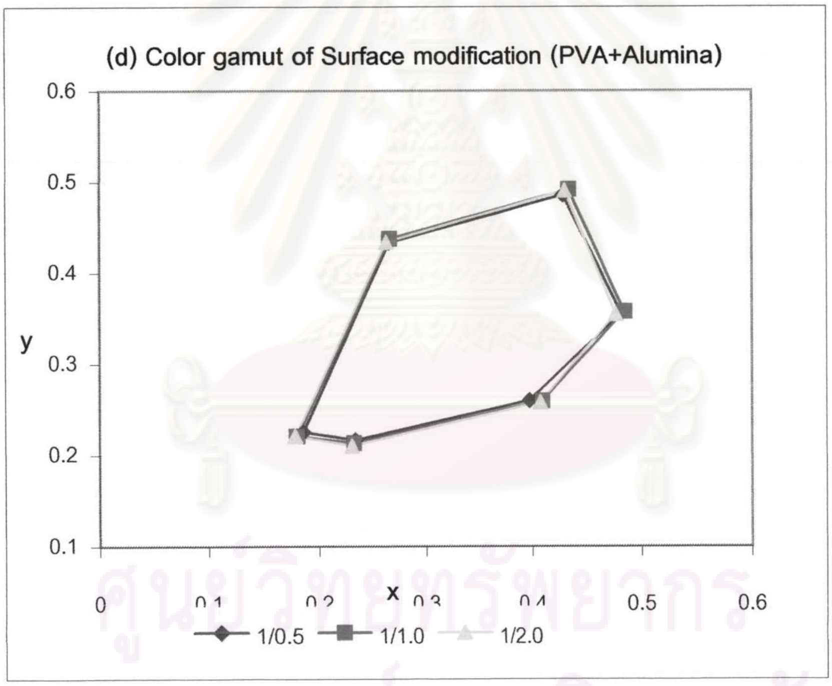


Figure 4-11(continued) Color gamut of the pigmented inkjet inks at different P/B ratios prepared by different dispersion technologies: (a) Polymer dispersion, (b) Surfactnt dispersion,(c) Micro-encapsulation and (d) Surface modification

Table 4-3 The gamut volume of inkjet inks with the different pigment dispersions

P/B ratio	Polymer dispersion	Surfactant dispersion	Micro-encapsulation	Surface modification
1/0.5	8959	8910	7518	8923
1/1.0	9104	9335	7576	9286
1/2.0	9421	9908	7767	9635

The color gamut volumes of the four types of pigment dispersion technologies on pre-treated cotton fabrics are listed in Table 4-3. The pigmented inkjet inks with 1/2 ratio has more volume than the others. We anticipate that ink viscosity in relation to its penetration play a vital role in the color gamut and color gamut volume of inks.

Penetration of a liquid flowing under its own capillary pressure in a horizontal capillary is described by the Lucas-Washburn equation.(45)

$$\ell = \left(\frac{r\gamma\cos\theta}{2\eta} \right)^{1/2} t^{1/2} \qquad (4.1)$$

where ℓ = penetration distance after time, t

r = pore radius

γ = surface tension

θ = contact angle

η = liquid viscosity

This equation shows that the high viscosity ink is infiltrated in the fabric slowly, so the ink is held on the top of the fabric. The more ink holdout, the higher the ink color gamut is found.

4.2.2 Air permeability

Air permeability is the ability of air to pass through a fabric. The most common permeability of fabrics to gases ever measured is that to air or wind. Obviously, wherever openings between the yarns or between fibers within the yarns are large, a good deal of air will pass through the fabric. All pigmented inkjet inks were printed on the treated cotton fabrics as shown Figure 4-12, the air permeability of the fabric as measured by the air permeability tester from Shirley varies from P/B ratio and pigment dispersion techniques.

As shown in Figure 4-12, it is apparent that increase in binder has little effect on air permeability. The ability of a fabric to resist air (low air permeability) or have air freely flowing through it (high air permeability) is dependent primarily on its thickness, porosity, configuration, geometry, type and amount of finish and coating.

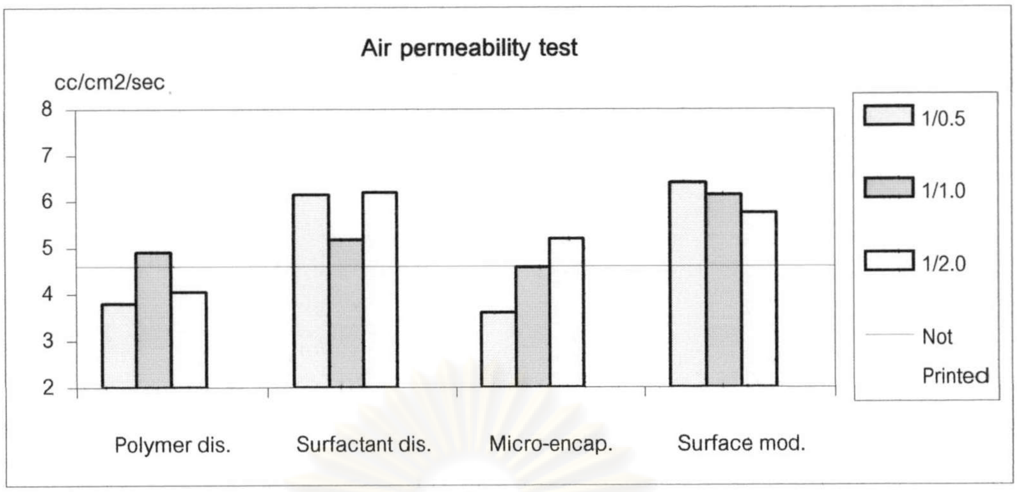
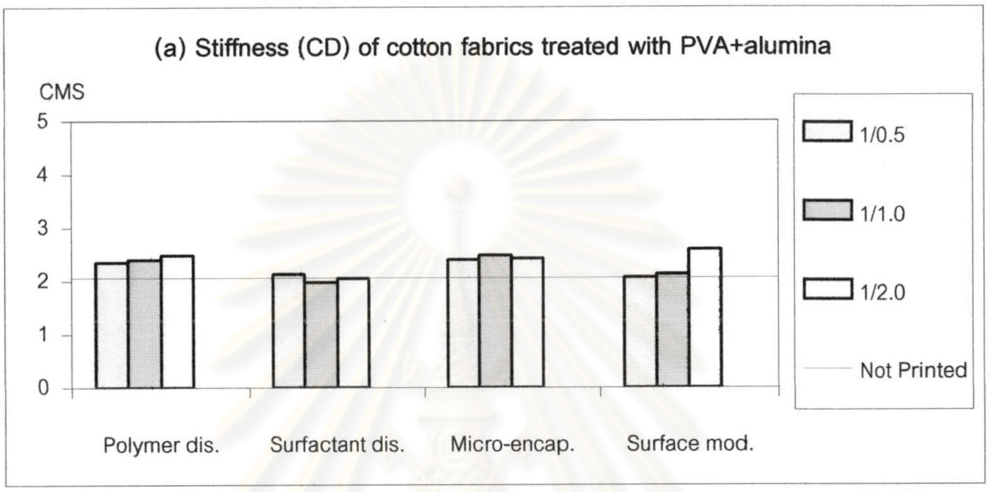


Figure 4-12 Air permeability test of the pigmented inkjet inks at different P/B ratios prepared by different dispersion technologies

4.2.3 Stiffness

The effect of pigment/binder ratio on stiffness properties of cotton fabrics are given in Figure 4-13, wherein the bending length is measured. Stiffness is the ability of a material to resist deformation. The higher bending length value means the higher stiffness of the fabric. In the case of a yarn subjected to a tensile force or pull, stiffness is thus the ability to resist elongation. Very importantly yarn directions as the cross-machine direction (CD) and machine direction (MD) are also measured. The term cross-machine direction is used to refer to the direction analogous to coursewise or filling direction in knitted or woven fabrics, respectively. Although all pigment/binder ratios of pigmented inkjet inks give the printed fabrics with acceptable hand. As for all of the printed cotton fabrics, the stiffness of the cross-machine direction is lower than those of the machine direction, because the density of filaments of the MD direction is higher than those of the CD direction (140x70 warp x filling).



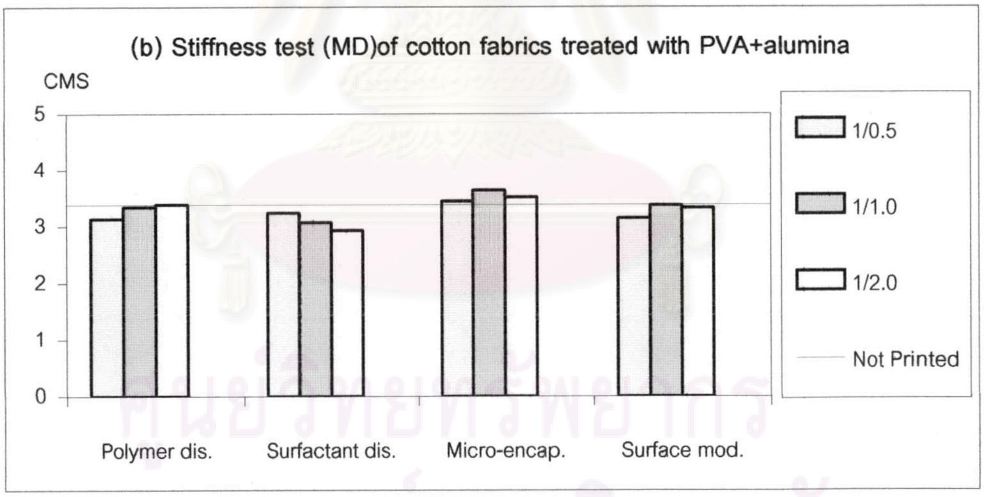
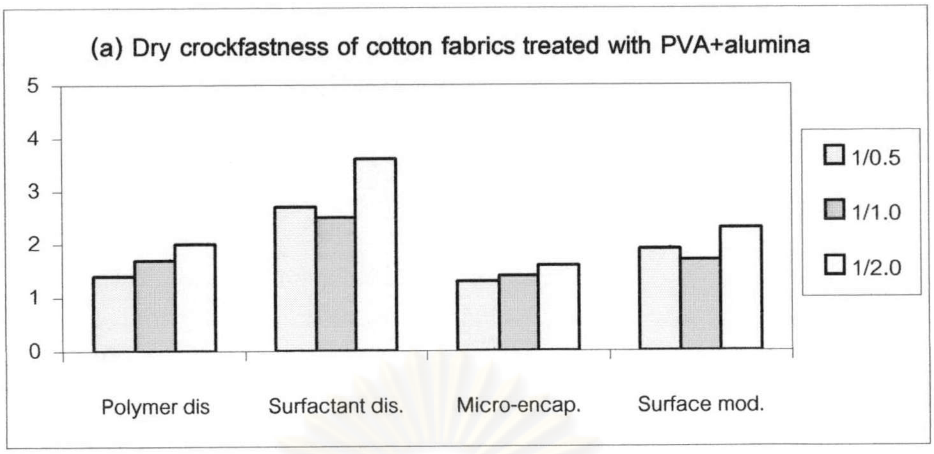


Figure 4-13 Bending length of the pigmented inkjet inks prepared by the different dispersion technologies for: (a) cross-machine direction (CD), and (b) machine direction (MD)

4.2.4 Crockfastness

Printed fabric properties of interest in the study were dry & wet crockfastness measured by a crockmeter, since some fabrics lose color through crocking, or rubbing against another fabric. Some fabrics crock when dry, some when wet, and some when both dry and wet. Two very interesting results shown in Figure 4-14 indicate that all four fabrics printed by the pigmented inkjet inks with different P/B ratios suffer from dry crockfastness and wet crockfastness. As expected, the level of both dry and wet crockfastness with increasing binder concentration at a fixed pigment concentration. Nonetheless, increasing concentration of the binder yields a better ink adhesion on the treated cotton fabrics.

Interestingly, the softer binder (low Tg, 283 K) containing inks produce a somewhat poorer crockfastness, especially the dry crockfastness is higher than the wet crockfastness.



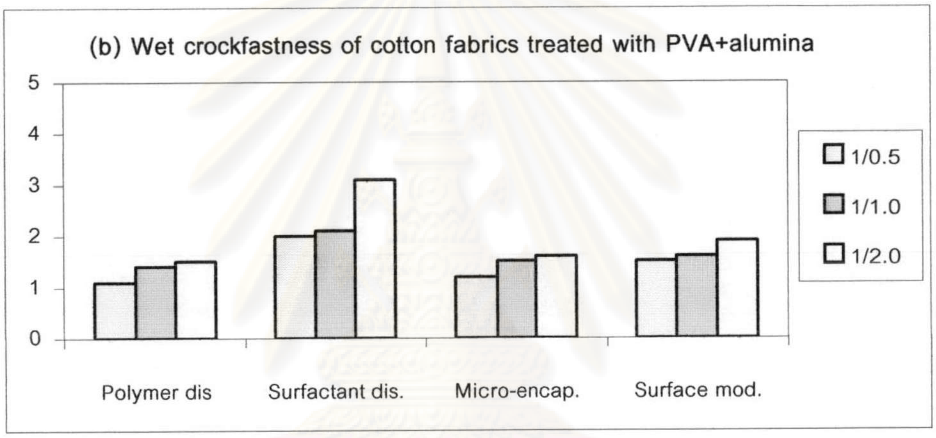


Figure 4-14 Crockfastness of the pigmented inkjet inks prepared by the different dispersion technologies : (a) dry crockfastness, and (b) wet crockfastness

We found that very fine pigment particles dispersed by polyester polymer dispersion, surfactant dispersion, micro-encapsulation and surface modification are the promising systems for uses in inkjet textile printing. Increasing binder concentrations for pigment hardly affect the ink surface tension, but increased the ink viscosity. Enhanced stability of the pigmented inkjet inks could be achieved by some additives of the inkjet inks. The pigmented inkjet inks produced with various pigment/binder ratios gave an acceptable printed fabric performance. Table 4-4 summarizes the best result of pigment/binder ratio for print evaluation.

4.3 Comparison of Pigment Dispersion Technique on the Properties of the Printed Cotton Fabrics

The four different pigment-based inks such as polymer dispersion, surfactant dispersion, micro-encapsulation, and surface modification were studied for print qualities. In this case, the ink containing the 1/2 pigment-to-binder ratio printed on treated cotton fabrics was investigated. Table 4-4 indicates that most of the best print qualities are resulted from the ink containing 1/2 pigment-to-binder ratio.

Table 4-4 Effect of pigment/binder ratio on printed fabrics printed by various pigment dispersion inkjet inks

Dispersion technique	Air permeability	Color appearance	Stiffness		Crockfastness	
			CD	MD	Dry	Wet
Polymer dispersion	1/1.0	1/2.0	1/0.5	1/1.0	1/2.0	1/2.0
Surfactant dispersion	1/0.5	1/2.0	1/1.0	1/2.0	1/2.0	1/2.0
Micro-encapsulation	1/2.0	1/2.0	1/0.5	1/0.5	1/2.0	1/2.0
Surface modification	1/0.5	1/2.0	1/0.5	1/0.5	1/2.0	1/2.0

4.3.1 Color Gamut and Color Gamut Volume

Color gamut and volume are the important colorimetric parameter. The four pigmented inks were printed on the treated cotton fabrics and the color gamut and its volume was evaluated as shown in Figure 4-15.

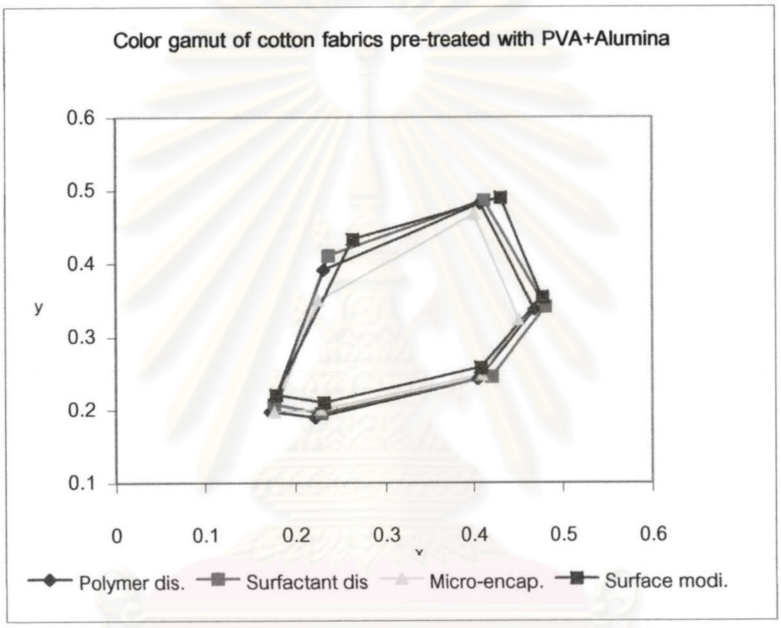


Figure 4-15 Color gamut of the pigmented inkjet inks with 1/2 ratio by different dispersion technologies

Figure 4-15 shows that the pigmented inkjet inks made from surfactant dispersion gave a wider color gamut, Table 4-3 shows higher color gamut volume than the inkjet inks prepared with the other pigment dispersion techniques.

The inks formulated with surfactant dispersions showed the higher gamut volume compared with inks using the dispersion with other dispersions as already mentioned in Table 4-3.

Aggregations on drying and fixing have a great effect on the purity of spectra and chroma. The ink made by pigment dispersion with surfactant prevented the aggregation on fixing. The pigment particles surrounded by an enough amount of surfactant show little aggregation on drying and give good wetting ability to textile fibers.

4.3.2 Air permeability

The amounts of air pass through a fabric printed with the inks made from surfactant dispersion and surface modification were higher than those from polymer dispersion, and micro-encapsulation. The inks formulated from surface modification yielded the highest air permeability because it did not contain any external polymer dispersant in the pigment dispersion.

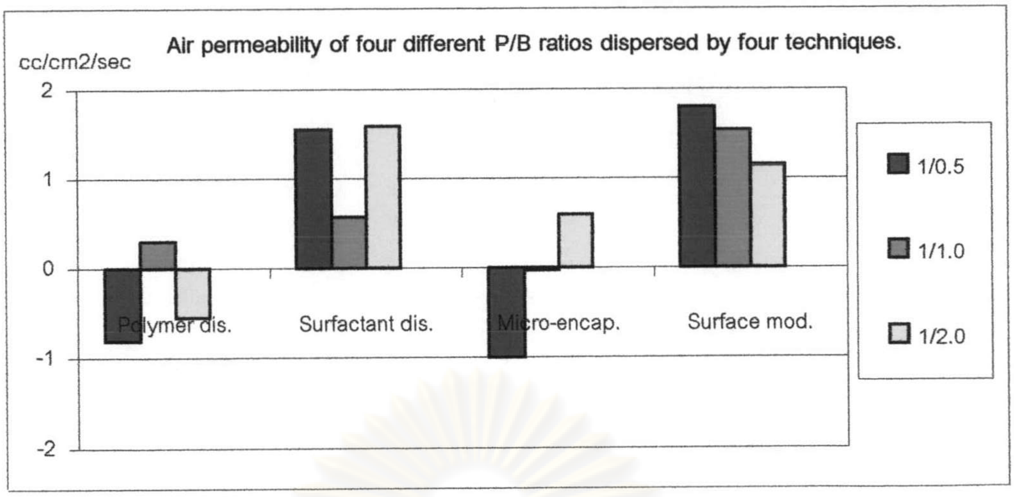
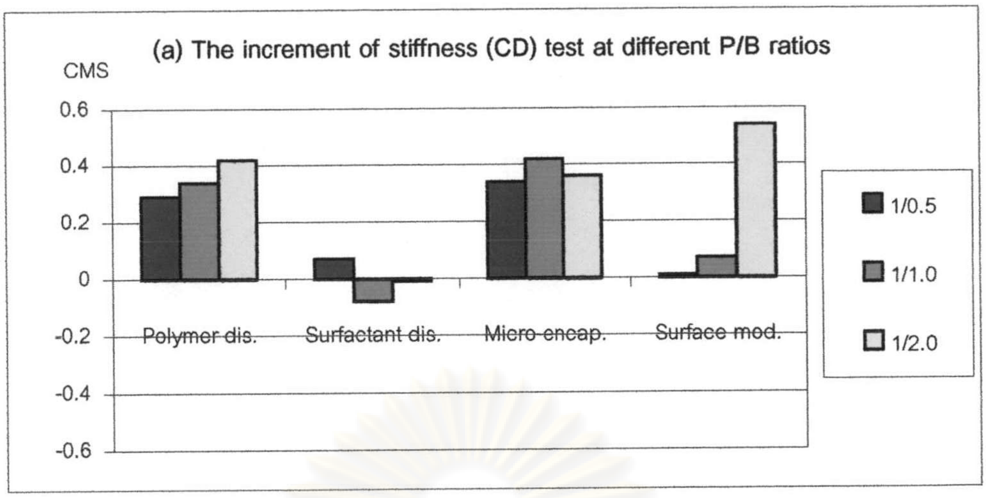


Figure 4-16 Air permeability of three P/B ratios dispersed by four dispersion techniques

4.3.3 Stiffness

The increment of bending length indicates the increase of bending length of the printed fabric after printing. Figure 4-17 shows that the printed cotton fabrics with the inks made from the surfactant dispersion had the lowest increment of the bending length, and the micro-encapsulated inkjet inks gave the highest increment of the bending length on both directions (CD and MD). In other words, the increased of stiffness of the printed fabric with surfactant dispersion showed the minimum increase, and the increase of stiffness of the printed fabric with micro-encapsulation technique showed the maximum increase.



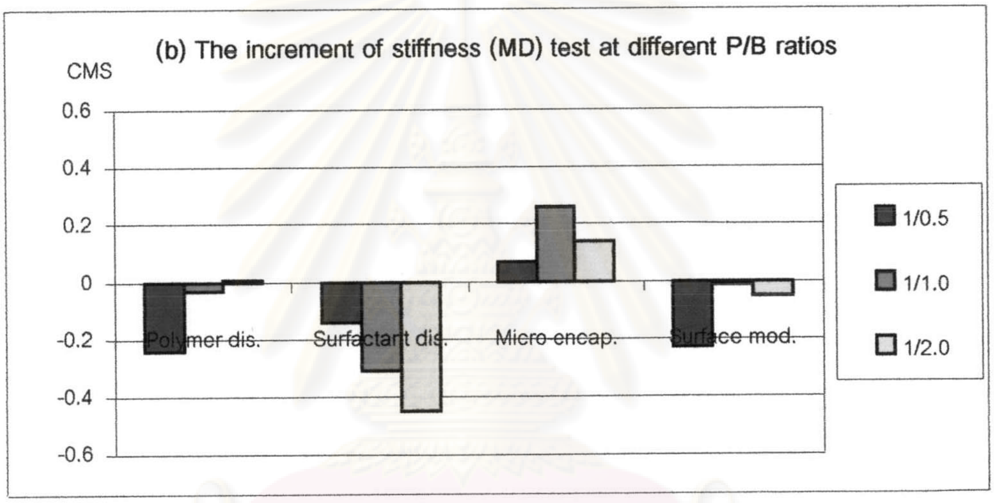


Figure 4-17 The change of stiffness caused by the P/B ratios in different pigment dispersion technologies in (a) cross-machine direction, and (b) machine direction (MD)

It is found that the higher amount of polymer for the pigment dispersion gave the high increment of bending length, or gave more stiffness of the printed fabrics. The micro-encapsulated pigments had the highest amount of polymer, so the printed fabric with this pigment increases the bending length when compared with the bending length of the fabric before printing.

4.3.4 Crockfastness

Figure 4-14 shows the crockfastness of pigmented inkjet inks prepared by the different dispersion technologies printed on the pre-treated cotton fabrics. The inks (4 inks) made from surfactant dispersion show higher dry and wet crockfastness than other inks from other dispersion techniques. The pigment particles of the latter inks (12 inks) largely remain on the surface with the limited ink spreading. The image can readily be smudged by rubbing the surface. The high crockfastness of printed fabrics with the surfactant dispersion was in a good combination to the polymer binder. On the contrary, the combination between the polymer dispersant in pigment dispersion and the polymer binder was not good, so the adhesion becomes weak.

To conclude the pigment dispersion technique on the printed fabric, we can point out a suitable dispersion technique for a particular property of the printed fabrics as shown in Table 4-5.

Table 4-5 Effect of pigment dispersion technique on properties evaluated from the printed fabrics

Property evaluated	Dispersion technique
Color gamut	Surfactant dispersion
Air permeability	Surface modification
Stiffness (CD)	Surfactant dispersion
Stiffness (MD)	Polymer dispersion
Dry crockness	Surfactant dispersion
Wet crockness	Surfactant dispersion

Very interestingly, the surfactant dispersion of the pigments produced most of the desired properties whereas polymer dispersion yielded the better stiffness on the machine direction of the fabric.

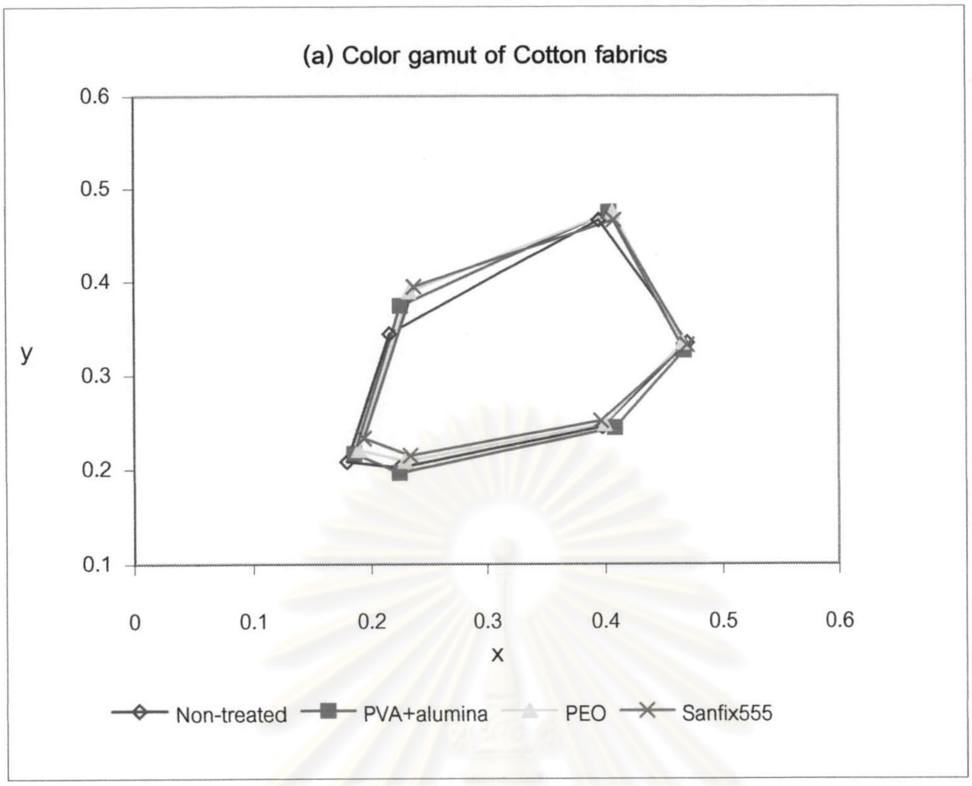
4.4 Effect of Pre-treatment on the Four Types of Fabric

Four types of fabrics: cotton, silk, polyester and cotton/polyester blend were pre-treated with three types of pre-treatment reagent: alumina dispersed in 10% poly(vinyl alcohol) solution, 3% poly(ethylene oxide) and sunfix 555 at 100% pick-up ratio of a padding method. After that, the untreated and pre-treated fabrics were printed using the 1/2 ratio of P/B containing inks by many polymer dispersion techniques. At the initial stage of printing, the nozzle was checked in order to examine the right-ejection of each individual cyan, magenta, yellow and black nozzle. These pigmented inkjet inks show the smooth and continuous lines indicating the best ink ejection and printability.

Finally, the printed fabrics were evaluated for color value, air permeability, bending length and wet&dry crockfastness as those in Section 4.2

4.4.1 Color Gamut and Color Gamut Volume

The printed colors of cyan, magenta, yellow, black, red, green, and blue on the untreated and pre-treated fabrics were measured. The color gamut was presented in a CIE x-y chromaticity diagram as shown in Figure 4-18, and the L*, a* and b* values were calculated the gamut volume was shown in Table 4-6.


(a) Color gamut of Cotton fabrics

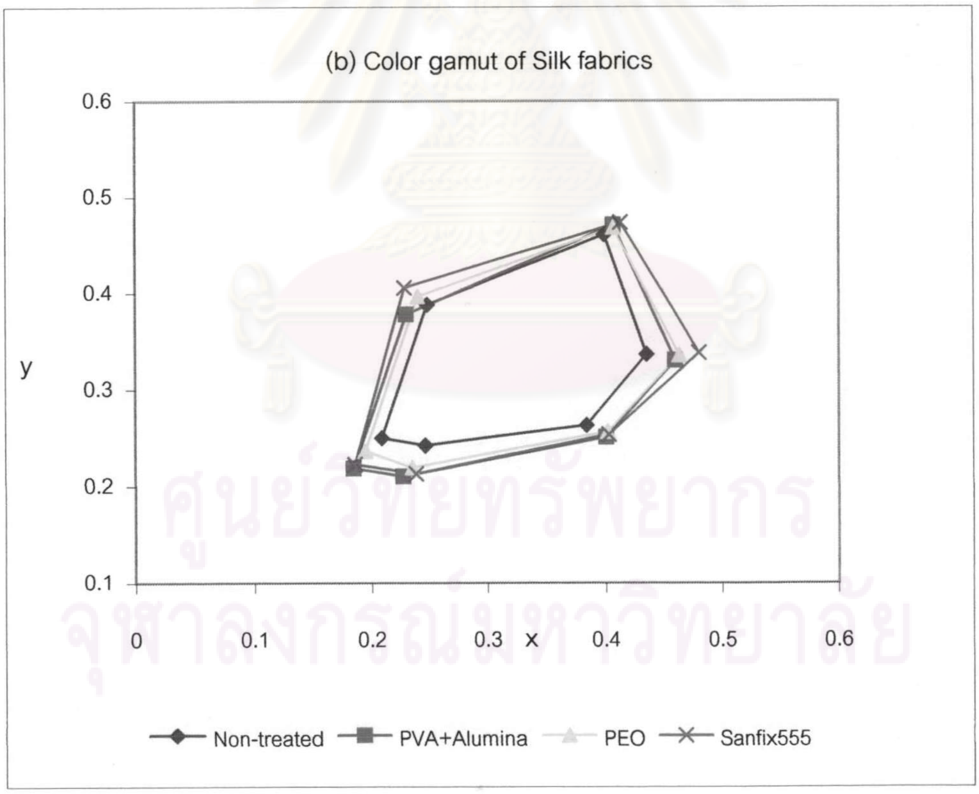
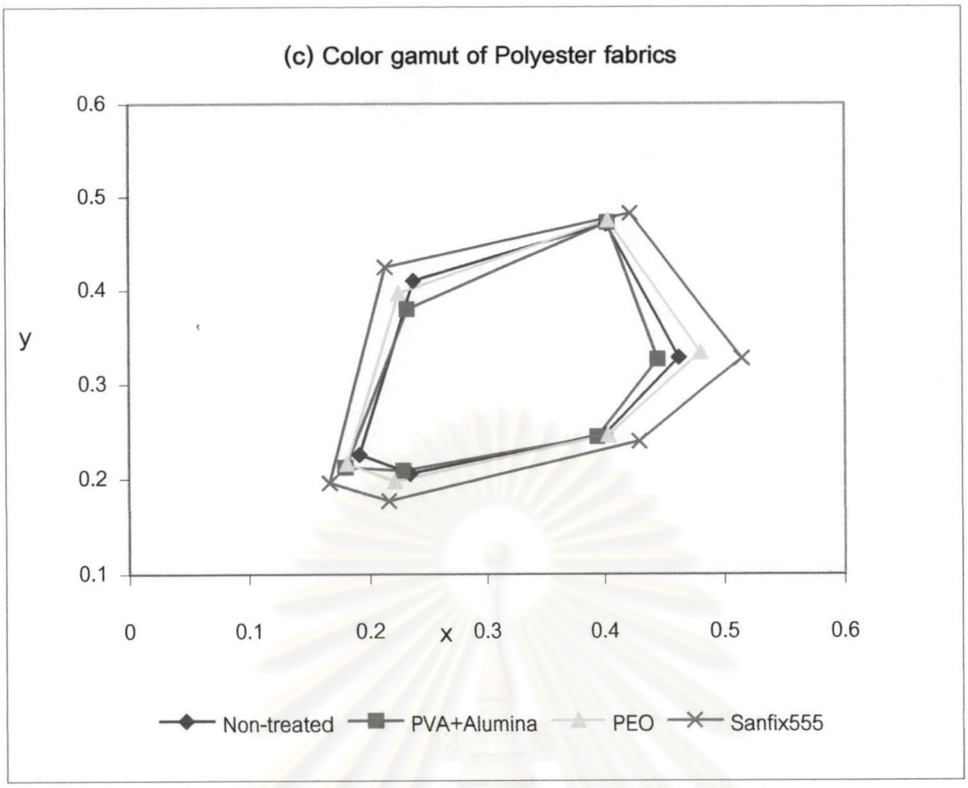

(b) Color gamut of Silk fabrics

Figure 4-18 Color gamut of the pigmented inkjet inks made from polymer dispersion with the different pre-treatment on different fabrics: (a) Cotton (b) Silk fabrics, (c) Polyester and (d) Blend fabrics..



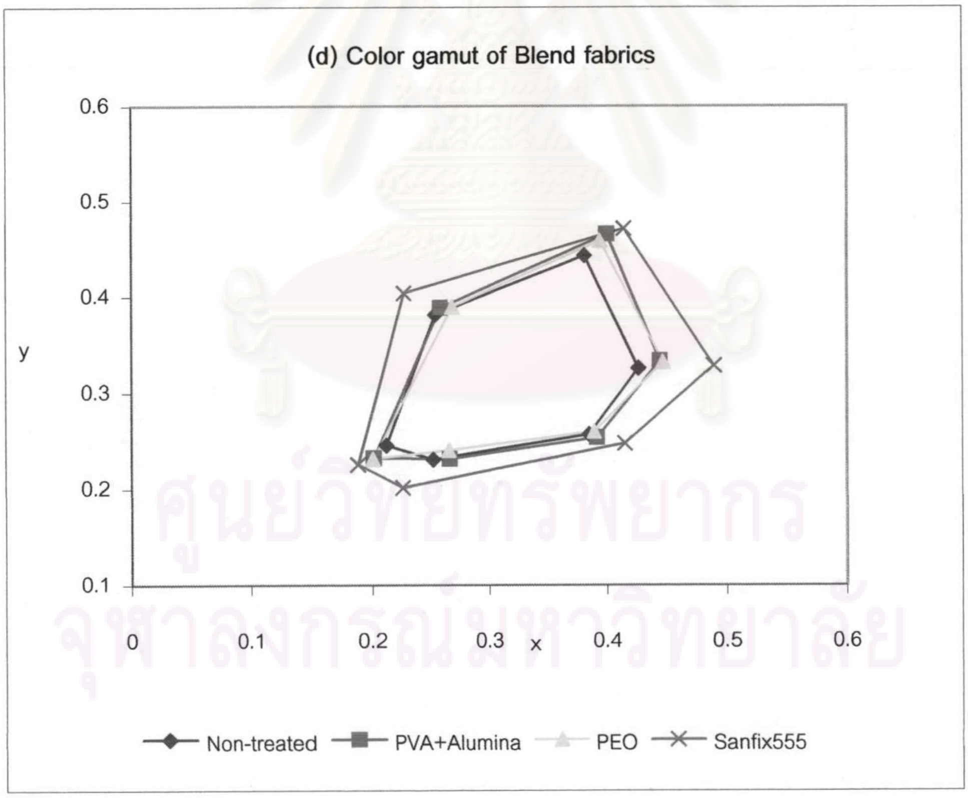


Figure 4-18 (continued) Color gamut of the pigmented inkjet inks made from polymer dispersion with the different pre-treatment on different fabrics: (a) Cotton, (b) Silk fabrics, (c) Polyester and (d) Blend fabrics..

Table 4-6 The gamut volume of inkjet inks printed on different fabrics with pre-treatment reagents

Fabric	Pre-treatment	Gamut volume
Cotton	Untreated	7306
	PVA + Alumina	8547
	PEO	8019
	Sunfix 555	5767
Silk	Untreated	4286
	PVA + Alumina	6584
	PEO	6405
	Sunfix 555	6905
Polyester	Untreated	7510
	PVA + Alumina	6911
	PEO	8000
	Sunfix 555	11124
Blend	Untreated	3134
	PVA + Alumina	5728
	PEO	5407
	Sunfix 555	6600

With the same printed fabrics, as shown in Figure 4-18 and Table 4-6, the color gamut and gamut volume of the pre-treated fabrics were better than the printed colors on the untreated fabrics. Basically for a good quality inkjet print, print through is not only a function of droplet penetration, but also of the light scattering property of the substrate used. The textiles printing has shown that when the ink has been jetted on fabric with a pick-up sufficiently high to achieve adequate penetration, there is a pronounced tendency for the ink to wick laterally along the individual yarns of the fabric. Control of the ink spread may be achieved, either by pre-coating the fabric with particulate products that increase the surface area for liquor adsorption or by mechanical action that renders the capillaries ineffective.(45) The pre-treatment exhibited higher color values because the pre-treatment reagent had been accepted on the fabric before excessive spreading of the inkjet inks and high swelling capacity took place, comparable with the fibrous material in retention of the ink. The pre-treatment on fabrics before printing is still necessary to prevent the entry of ink liquid to the capillary spaces and increase the availability of surface area for the drops rapidly permeating into the fabric.(46) The amount of the pigment on the surface of pre-treated fabric was more than the amount of the pigment on the surface of the untreated fabric, therefore the color performance of the pre-treated fabric was better than the untreated fabric.

Obviously, the printed cotton fabrics, pre-treated with an aqueous dispersion of poly(vinyl alcohol) and alumina, gave the best result of color performance, whereas the silk, polyester and cotton-blend-polyester fabrics, pre-treated with sunfix 555 (cationic acrylate polymer), gave the best color value. The reason might be that the pre-treatment reagent, cationic acrylate polymer, has a large amount of cations in the molecular structure, the interaction between the cations from pre-treatment reagent and the anions from pigment dispersion gave the good fixing and a higher color value. Poly(ethylene oxide) is a neutral polymer, having neither cations nor anions, so the color value of printed fabric padded with PEO was, of course, poor. The last pre-treatment reagent is poly(vinyl alcohol) and alumina mixed solution flattened the fibers increasing the surface area of the substrate and reducing the amount of open inter-fiber spaces available.

The polyester fabric, pre-treated with the cationic polymer, gave the highest gamut volume as shown in Table 4-6, the polyester fabric is hydrophobic, it did not absorb water. The formation of a thin polymer film over the surface of the substrate prevents the entry of liquid to the capillaries, in which the polymer film's swelling rate is higher than the ink absorption rate of the substrate.(46)

4.4.2 Air permeability

The air permeability of the pre-treated and printed fabrics of cotton, silk, polyester and cotton/polyester blend fabrics was observed. The air permeability of the non-printed fabric was not different from that of the printed fabrics, so the air permeability value depends on the pre-treatment reagent as shown in Table 4-7.

Table 4-7 Dependence of pre-treatment reagent on air permeability of four types of fabric.

Type of Fabric	Pre-treatment reagent			
	Untreated[a]	PVA+Alumina	PEO	Sunfix 555
Cotton	9.02	2.39	10.37	9.88
Silk	12.68	2.51	28.86	16.43
Polyester	29.41	3.04	55.42	38.11
Cotton/Polyester	50.33	37.06	48.92	46.21

[a] There is no difference of air permeability of the fabrics before and after printing

Table 4-7 shows that the pre-treatment with the solution of PVA mixed with alumina decreases the air permeability of the fabric. However, the treated fabrics with poly(ethylene oxide) increase the ability of air to pass through a printed fabric.

4.4.3 Stiffness

The four untreated fabrics of cotton, silk, polyester, and cotton/polyester blend were each treated with PVA+Alumina, PEO, and Sunfix555. Each treated fabric was printed with the inkjet inks made from polymer dispersion. The inks did not affect the stiffness value. The bending length also depends on the pre-treatment reagent of the fabric. The bending lengths of the treated fabrics were investigated, which results on both CD and MD are shown in Tables 4-8 and 4-9.

Table 4-8 Effect of pre-treatment reagents on bending length values at CD before printing.

Type of Fabric	Pre-treatment reagent			
	Untreated	PVA+Alumina	PEO	Sunfix 555
Cotton	1.57	1.91	1.54	2.2
Silk	1.28	1.57	1.94	1.66
Polyester	1.08	2.52	2.84	3.11
Cotton/Polyester	1.81	3.18	3.39	4.06

Table 4-9 Effect of pre-treatment reagents on bending length values at MD before printing.

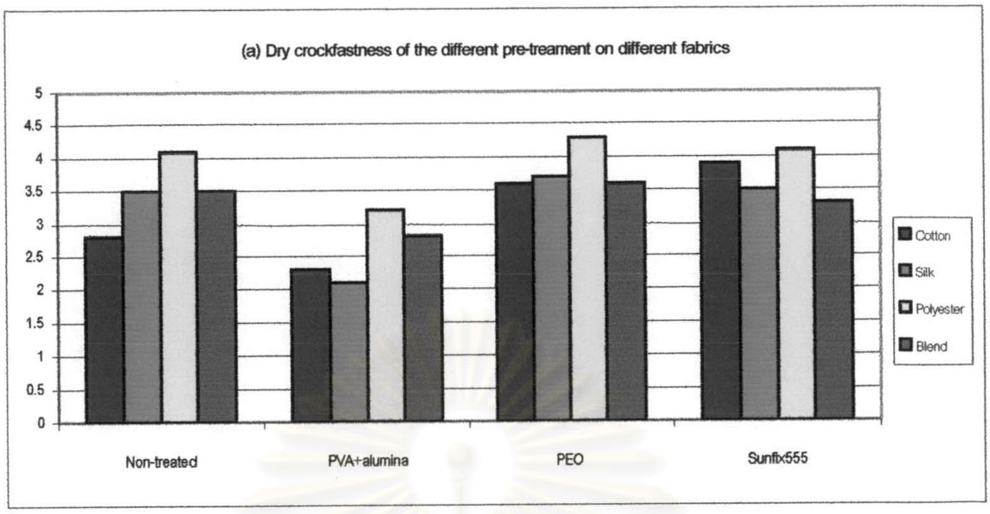
Type of Fabric	Pre-treatment reagent			
	Untreated	PVA+Alumina	PEO	Sunfix 555
Cotton	2.01	2.84	2.28	2.78
Silk	2.34	2.91	2.66	2.83
Polyester	1.44	2.96	2.88	3.44
Cotton/Polyester	1.83	3.29	3.64	4.55

Tables 4-8 and 4-9 show that the bending lengths of the printed cotton and silk fabrics, each treated with PVA+Alumina, PEO and Sunfix 555 did not show a significant difference. On the other hand, polyester and cotton/polyester blend fabrics could not absorb the polymers in the pre-treatment reagents, as a result of the increased bending length compared with the untreated fabrics.

4.4.4 Crockfastness

Figure 4-19 shows that crockfastness of the printed fabrics without treatment and with three pre-treatment reagents. The printed fabrics, pre-treated with PEO and Sunfix 555 show the higher dry crockfastness than the printed fabrics, pre-treated with PVA+alumina of about 1 unit of crockfastness level. The high crockfastness of the printed fabrics with PEO was caused by the low ink pick-up at the surface of the fabric, whereas the crockfastness of the printed fabrics with sunfix 555 contributed a good fixing by an interaction between the cationic acrylate polymer and anionic pigment. Good adhesion of the printed fabric, pre-treated with PEO and Sunfux 555, showed the high level of dry crockfastness.

As expected, the printed fabrics render a lower wet crockfastness as a direct attribute from their pretreatment reagents of a hydrophilic nature, which is relatively water soluble.



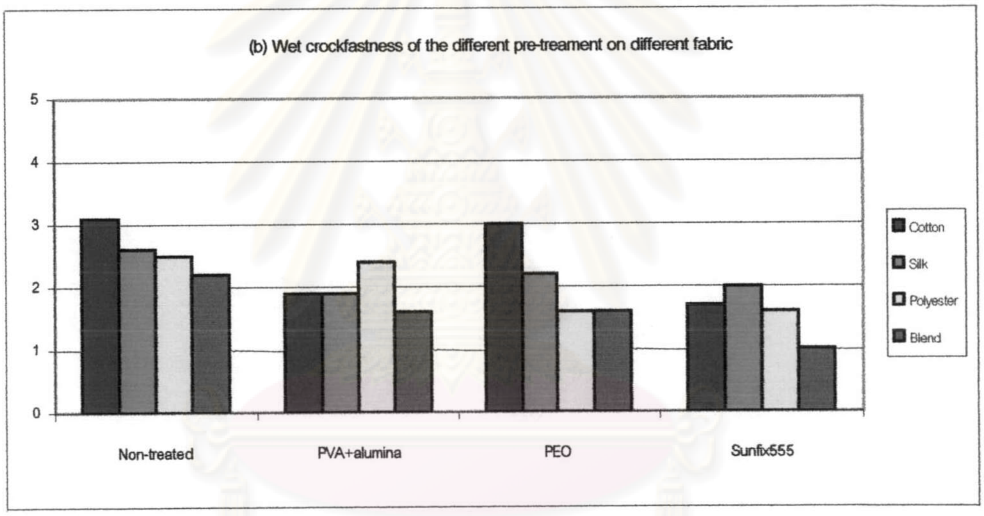
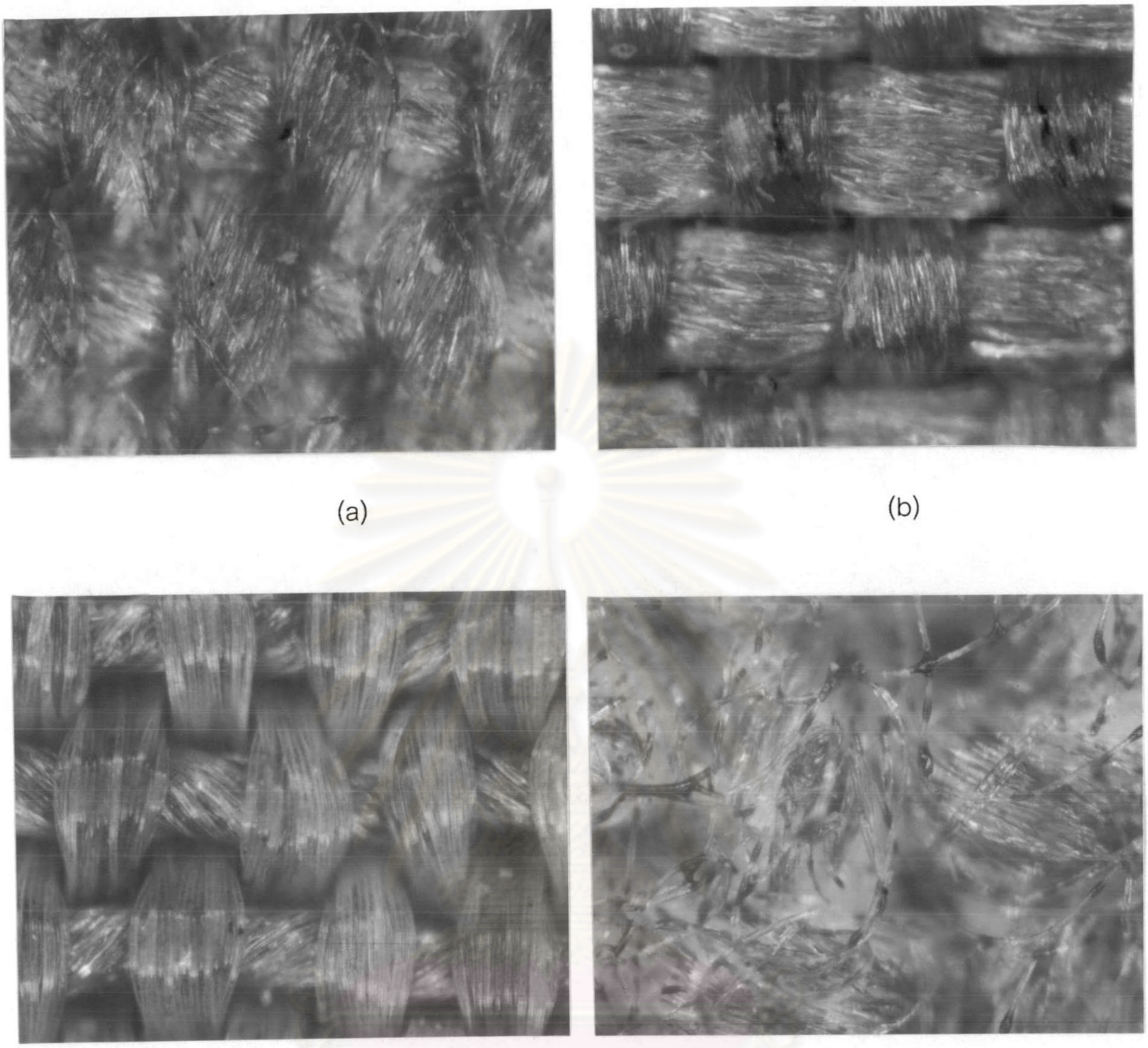


Figure 4-19 Crockfastness of three pre-treatment reagents on four fabrics: (a) dry crockfastness, and (b) wet crockfastness

The printed polyester fabrics for each pre-treatment show the highest crockfastness than other printed fabrics, because the low ink hold out at the surface of the fabric owing to more inkjet ink penetrating into the fabric as shown in Figure 4-20. The more the amount of ink on the surface, the lower the crockfastness level.



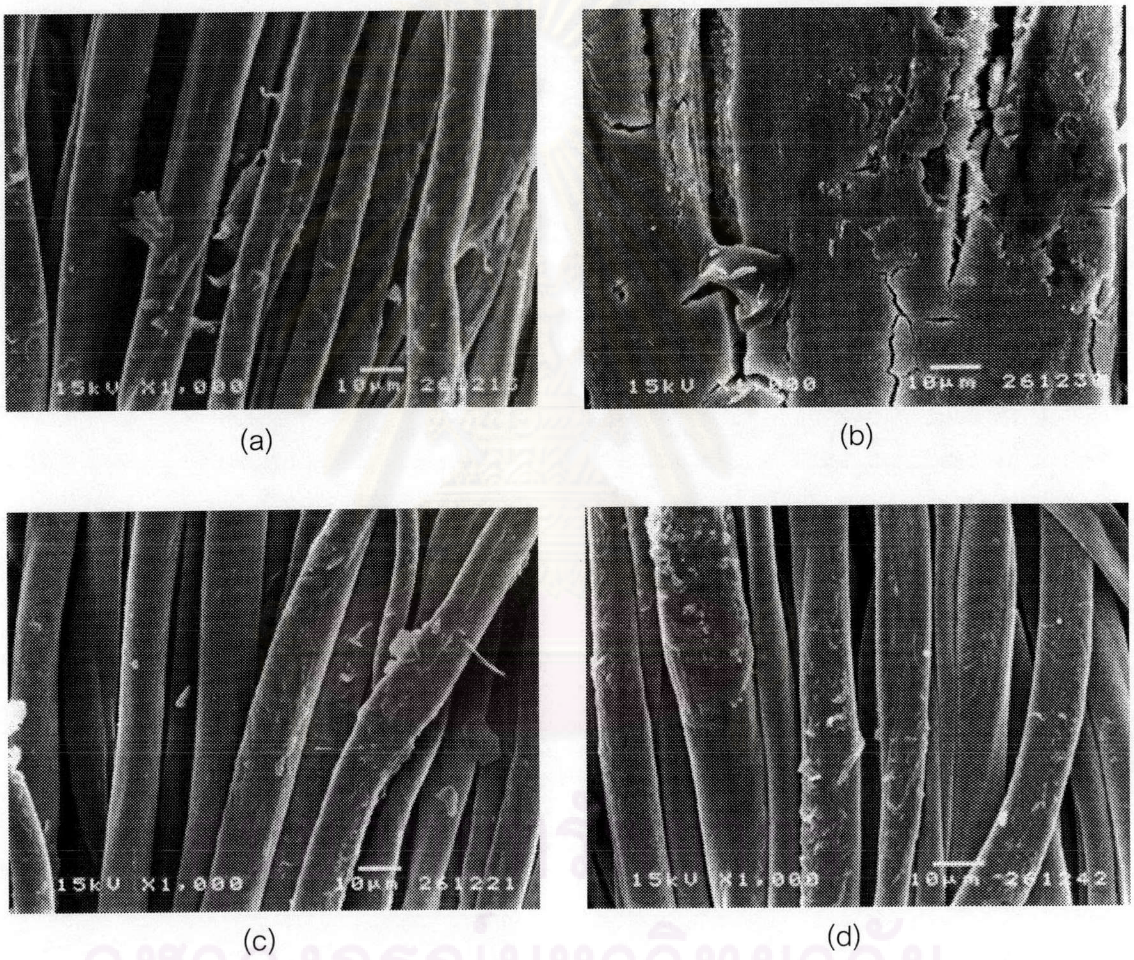
(a) (b)

(c) (d)

Figure 4-20 Optical photograph of the printed fabrics without pretreatment (a) cotton fabric, (b) silk fabric, (c) polyester and (d) cotton/polyester blend (x10)

4.4.5 Morphology of the Fabrics

As mentioned in Section 4.4.4, the four fabrics treated with the three pre-treatment reagents were subject to morphology analysis by scanning electron microscrope as shown in Figures 4-21 to 4-24.

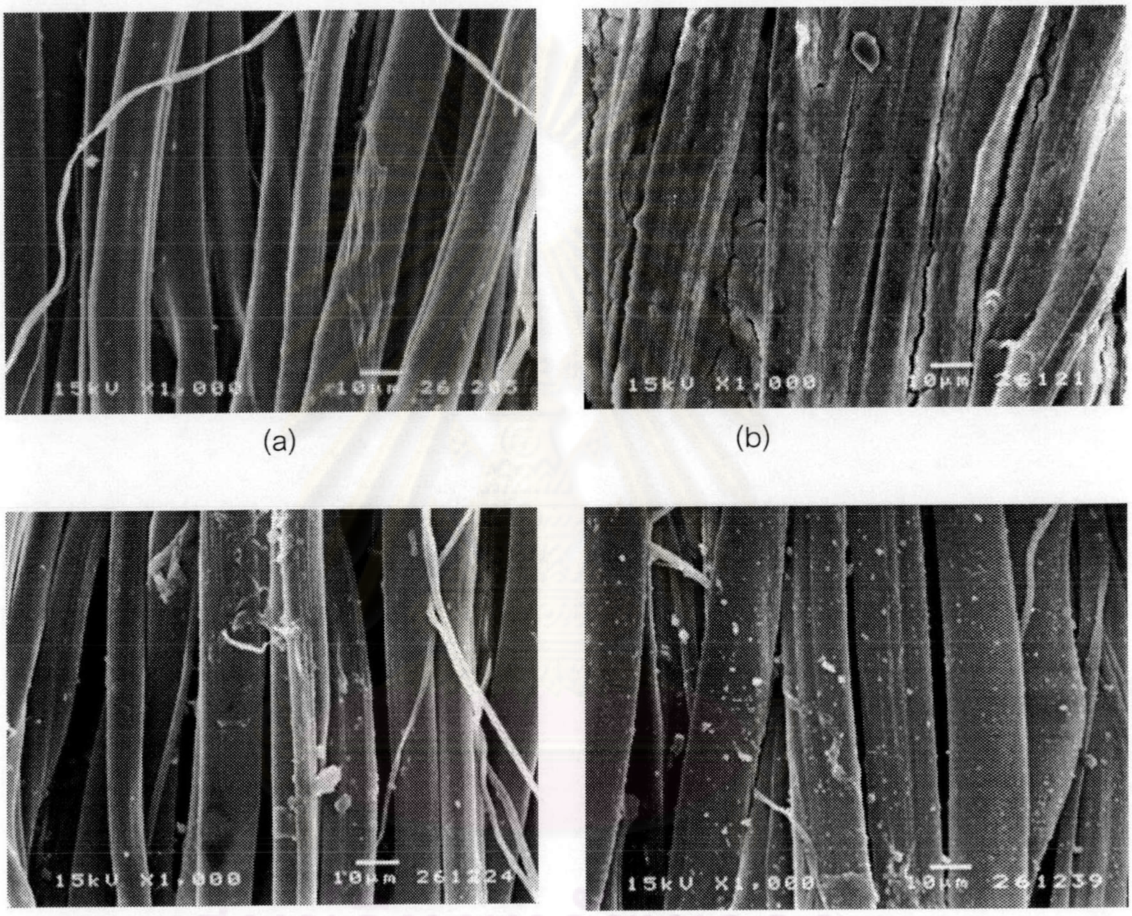


(a) (b)

(c) (d)

Figure 4-21 SEM of cotton fabrics with three pre-treatment reagents: (a) without treatment, (b) PVA+alumina, (c) PEO, and (d) Sunfix 555 (x1000)

Like all cellulose fibers, cotton contains carbon, hydrogen, and oxygen atom and reactive hydroxyl (OH) groups. The molecular chains are in a spiral form as shown in Figure 4-21 (a).

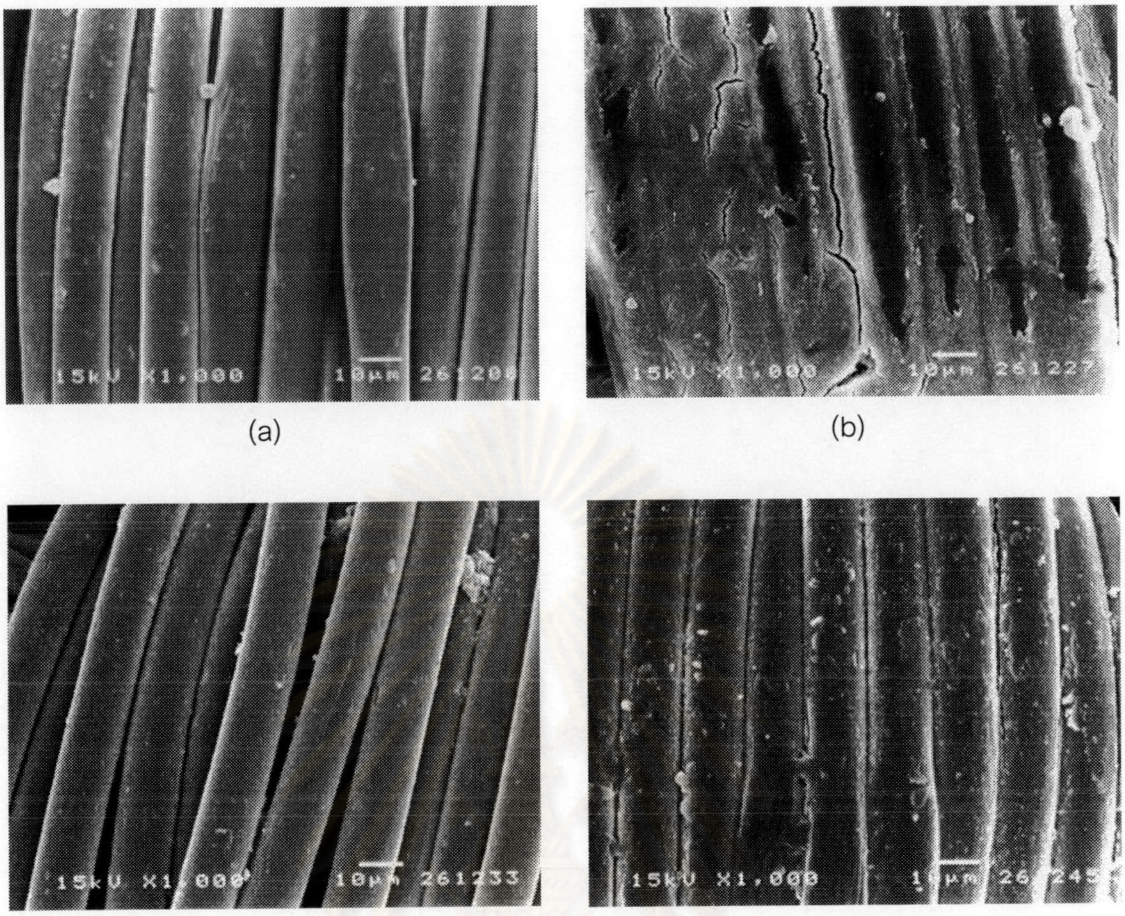


(a) (b)

(c) (d)

Figure 4-22 SEM of silk fabrics with three pre-treatment reagents: (a) without treatment, (b) PVA+alumina, (c) PEO, and (d) Sunfix 555 (x1000)

Silk is a natural continuous filament fiber. It is a solid fiber, smooth but irregular in diameter along its shaft as shown in Figure 4-22 (a). Silk fibroin contains CHON in polypeptide chains.

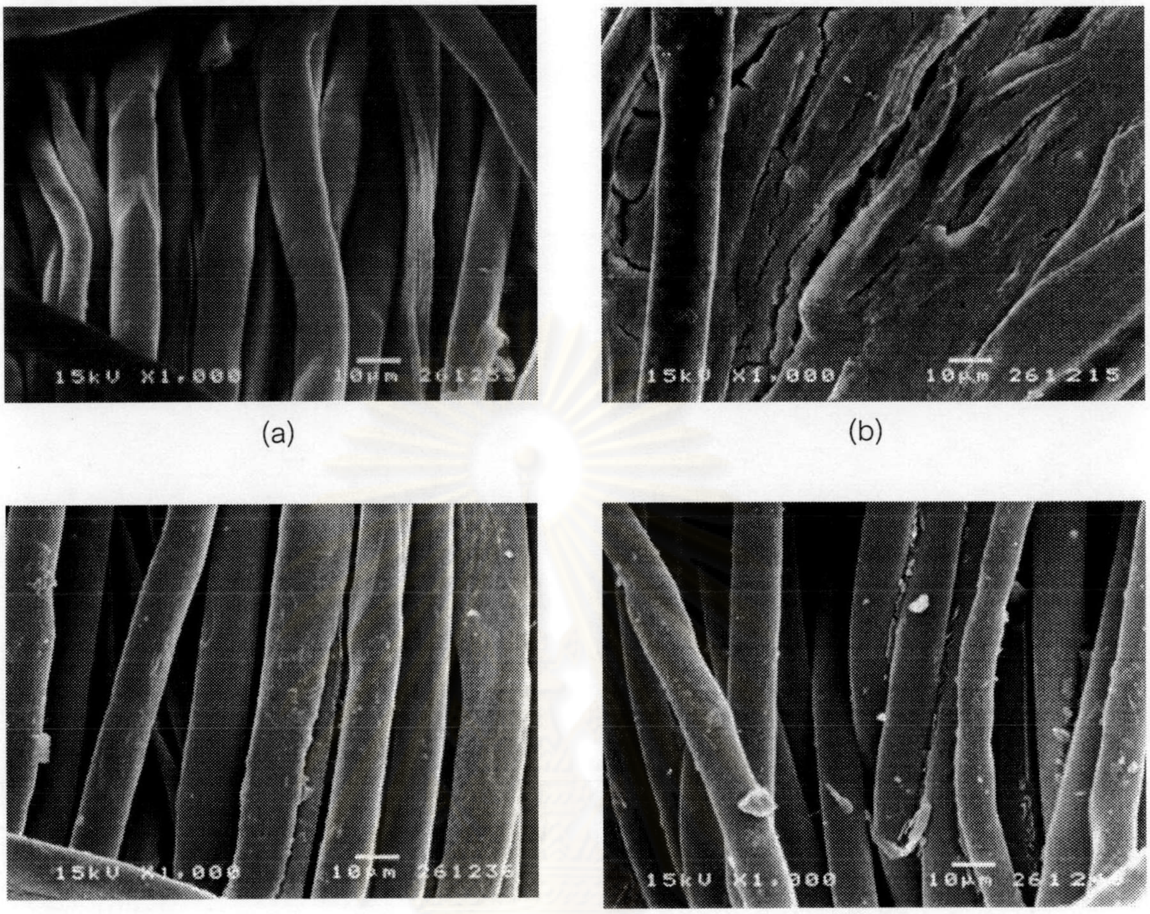


(a) (b)

(c) (d)

Figure 4-23 SEM of polyester fabrics with three pre-treatment reagents: (a) without treatment, (b) PVA+alumina, (c) PEO, and (d) Sunfix 555 (x1000)

Polyester is made by reacting an acid with an alcohol. Filaments are high tenacity or regular as shown in Figure 4-23 (a).



(a) (b)

(c) (d)

Figure 4-24 SEM of cotton/polyester blend fabrics with three pre-treatment reagents: (a) without treatment, (b) PVA+alumina, (c) PEO, and (d) Sunfix 555 (x1000)

Figures 4-21 to 4-24 show that the pre-treatments increase the available surface area of the substrate, so the amount of the pigment on the surface of pre-treated fabric was more than the amount of the pigment on the untreated fabric, therefore the color performance, color gamut and color volume of the pre-treated fabric was better than the untreated fabric.

Figures 4-21 (b) to 4-24 (b) show that the pre-treatment on the fabrics could lead to the formulation of film over the surface of the substrate covering the spaces between fibers and blocking of the inter-fiber spaces with large particles. The cationic pigment (PVA and alumina mixed solution) decrease the air permeability on the different fabrics due to the thick film layer over the surface of fabrics. The thick layer of deposits encircling the fibers and filling the fiber interstices.

The aqueous polymer, poly(ethylene oxide), the density of the deposits is not as high, but due to the nature of the fabric structure, the deposits contribute to the constriction of the inter fiber spaces as shown in Figures 4-21 (c) to 4-24 (c). Therefore, the fabric treated with aqueous polymer gave the best result of the air permeability.

Figures 4-21 (d) to 4-24 (d) show that the cationic acrylate polymer (Sunfix 555) treated on fabric flattened the fibers increasing the surface area of the substrate and reducing the amount of the open inter-fiber spaces available.

To conclude the pre-treatment reagent on four types of fabric printing with the pigmented inkjet inks made from the polymer dispersion, we can point out a suitable pre-treatment reagent for a particular property of the printed fabric as shown in Table 4-10.

Table 4-10: Effect of four pre-treated fabrics printed by the pigmented inkjet inks

Type of fabric	Color gamut	Air permeability	stiffness		crockfastness	
			CD	MD	Dry	Wet
Cotton	PVA+alumina	PEO	PEO	untreated	Sunfix	untreated
Silk	Sunfix 555	PEO	untreated	untreated	Sunfix	untreated
Polyester	Sunfix 555	PEO	PEO	untreated	Sunfix	PVA
Blend	Sunfix 555	PEO	untreated	untreated	PEO	untreated

Very interestingly, the cationic acrylate polymer (Sunfix 555) reagent produced the better printed color and dry crockfastness, whereas the poly(ethylene oxide) treatment yielded the better air permeability and stiffness on the cross-machine direction (CD) of the printed fabric.