CHAPTER 3

EXPERIMENTAL

3.1 Materials

3.1.1 **Colorant** (Cyan, Magenta, Yellow and Black): four types of pigment dispersion technique were used:

3.1.1.1 **Polyester polymer dispersion:** water-based dispersion of pigment and polymers from Dainichiseika Color and Chemicals Mfg Co., Ltd. Toyko, Japan.

S-7 C-17: C.I. Pigment Blue 15:4

S-7 M-12: C.I. Pigment Red 122

S-7 Y-20: C.I. Pigment Yellow 138

S-7 K-5: C.I. Pigment Black 7

Ingredients of the polymer dispersion are organic pigment (9-11%), polymer dispersing agent (2-3%), organic solvents (10-11%), additives (<2%) and water (75-76%).

3.1.1.2 **Surfactant dispersion:** water-based pigment from Fuji Pigment Co., Ltd. Hyogo, Japan.

SP BI 6447: C.I. Pigment Blue 15:3

SP M 9345: C.I. Pigment Red 122

SP Y 4254: C.I. Pigment Yellow 138

SP Bk 8769: C.I. Pigment Black 7

Ingredients of the surfactant dispersion are pigment (12-18%), dispersant (3-5%), organic solvents (6-12%) additives (0.3%) and water (64-78%)

3.1.1.3 **Micro-encapsulation:** micro-encapsulated pigments from Dainippon Ink and Chemicals,Inc. Tokyo, Japan.

MCC-146-K60C: C.I. Pigment Blue 15:4

MCM-146-K59C: C.I. Pigment Red 122

MCY-146-K61C: C.I. Pigment Yellow 128

MCB-146-K62C: C.I. Pigment Black 7

Ingredients of micro-encapsulated pigment are pigment (6-15%), encapsulation polymer (5-14%), organic solvents (25%), additives (0.8%) and water (45-64%)

3.1.1.4 **Surface modification:** surface modified pigments from Cabot Corporation, Massachusetts, USA.

Cyan (IJX 253) : C.I. Pigment Blue 15:4

Magenta (IJX 266) : C.I. Pigment Red 122

Yellow (IJX 273) : C.I. Pigment Yellow 74

Black (CAB-O-JET200) : C.I. Pigment Black 7

Ingredients of the surface-modified pigment are pigment (10-19%), organic solvents (6-12%), additives (2%) and water (68-80%)

3.1.2 **Polymer binder**: one type was used: NK binder A-12 (acrylic emulsion) from Shin-Nakamura Chemical Co, Ltd. Wakayama, Japan.

Physical data: pH 6.5

Viscosity (25^{o}C) >100 mPa s

Non-volatile 45%

Appearance is milky white emulsion and mild odor

Detailed information of pigment dispersion and binder is presented in Table 3-1.

Table 3-1 Properties of pigment dispersions and binder[44]

Chemical	Color Index of pigment (CI)	Chemical class Of pigment	Pigment Conc. (wt. %)	Particle size (nm)	pH	Vis (mPa s)
Polymer dispersion of Cyan : S-7 C-17	PBI 15:4	Copper Phthalocyanine	9.5	112	8.0	2.4
Magenta : S-7 M-12	PR 122	Quinacridone	9.7	113	8.0	2.7
Yellow : S-7 Y-20	PY 138	Quinophthalone	9.7	95	7.8	2.2
Black : S-7 K-5	PBk 7	Carbon black	10.1	74	7.2	2.4
Surfactant dispersion of Cyan : SP BI 6447	PBI 15:3	Phthalocyanine	18	111	9	3.4
Magenta : SP M 9345	PR 122	Quinacridone	14	122	8.5	3.5
Yellow : SP Y 4254	PY 138	Quinophthalone	12	83	8.7	2.8
Black : SP Bk 8769	PBk 7	Carbon black	15	94	8.6	7.8
Micro-encapsulation of Cyan : MCC-146-K60C	PBI 15:3	Phthalocyanine	14.3	111	9.3	4.0
Magenta : MCM-146-K59C	PR 122	Quinacridone	13.9	136	9.1	4.6
Yellow : MCY-146-K61C	PY 128	Diazo condensation	14.3	128	10.3	16.9
Black : MCB-146-K62C	PBk 7	Carbon black	6	79	9.2	3.5
Surface modification of Cyan : C (IJX 253C)	PBI 15:3	Phthalocyanine	10.7	91	6.9	2.1
Magenta : M (IJX 266D)	PR 122	Quinacridone	10.5	105	7.6	2.4
Yellow : Y (IJX 273B)	PY 74	Monoazo; Acetoacetyl	10.9	137	6.4	2.3
Black : Bk (CAB-O-JET 200)	PBk 7	Carbon black	19.9	128	7.9	4.3
NK A-12 binder	-	Polyacrylate	45	111.2	6.5	>100

3.1.3 Solvents:

3.1.3.1 **Ethylene glycol** ($C_2H_6O_2$) from Merck, Darmstagt, Germany, analytical grade, M = 62.07 g mol^{-1}

3.1.3.2 **Glycerin** ($C_3H_8O_3$) from Merck, Darmstagt, Germany, analytical grade, M = 92.10 g mol^{-1}

3.1.4 **Additive**: surfactant, urea and sodium hydroxide were used

The surfactant employed was supplied by Nikko Chemicals Co. Ltd., there was polyoxyethylene (30) cetyl ether used as a nonionic surfactant.

3.1.5 **Pre-treatment polymer**: three types were used:

3.1.5.1 **Cationic pigment dispersion**:

10% Poly(vinyl alcohol)+10% Alumina

Poly(vinyl alcohol) : PVA 205 from Siam Chemicals & Resins Co., Thailand, 86-89 % hydrolysis, Degree of polymerization 1000

Alumina (AEROSIL MOX170) from AEROSIL NIPPON, Japan

Particle size of 200 nm was found by the current measurement.

3.1.5.2 **Cationic polymer**: from Sanyo Chemical Industries, Ltd. Kyoto, Japan

10% Sunfix 555 (cationic acrylate polymer), whose structure is as follows:

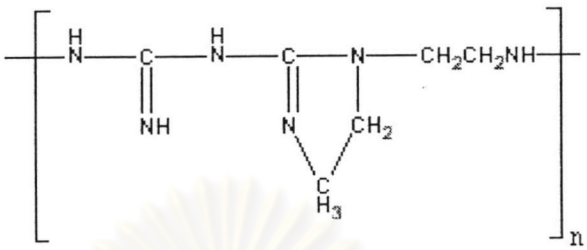


Figure 3-1 Chemical structure of cationic acrylate polymer (Sunfix 555)

3.1.5.3 **Aqueous polymer:** from Meisei Chemical works, Ltd., Tokyo, Japan

3% Poly(ethylene oxide): High molecular weight (2,000,000-3,000,000 dalton units)

3.1.6 **Fabric:** four types of bleached fabric and without optical brightening agent were used:

3.1.6.1 **Cotton fabric:** plain weave, construction 140x75, 130 g/m^2 (by current measurement)

3.1.6.2 **Silk fabric:** plain weave, construction 82x85, 104 g/m^2 (by current measurement)

3.1.6.3 **Polyester fabric:** plain weave, construction 136x90, 130 g/m^2 (by current measurement)

3.1.6.4 Cotton/polyester (35/65) blend fabric: plain weave, construction 54x60, 150 g/m^2 (by current measurement)

3.2 Apparatus

3.2.1 Inkjet printer for the pigment system printed on textile: EPSON Stylus Color 3000, Seiko Epson corporation, Nagano, Japan

3.2.2 Viscometer: Brookfield DV III Programmable Rheometer/TC500, Brookfield Engineering Laboratories, Inc., Stoughton, USA

3.2.3 Surface tensiometer: K 8, Kruss, Germany

3.2.4 Zetasizer: model 4, Malvern, USA

3.2.5 Light scattering, Auto sizer, Malvern, USA

3.2.6 Image analyzer: LUZEX F, PM 10-AD, Olympus, Nireco Corporation, Tokyo, Japan

3.2.7 Scanning Electron Microscope (SEM): JSM 6400, JEO, Tokyo, Japan

3.2.8 pH meter: SA 720, Orion Research Incorporation, Boston, USA

3.2.9 Drying oven: 6-2 FI, Rapid Labortex Corporation, Taiwan

3.2.10 Mechanical Homogenizer: T. K. ROBO MICS, Tokushu Kika Co., Ltd., Osaka, Japan

3.2.11 Machanical stirrer: RE 16, IKA-Labortechnix, Germany

3.2.12 Spectrophotometer: Digital Swatchbook, X-Rite Incorporation, Michigan, USA.

3.2.13 Crockmeter: AATCC Crockmeter, Atlas Electric Devices Corporation, Chicago, USA

3.2.14 Centilever Stiffness Tester: Sherley Development Limited, England

3.2.15 Air permeability tester: Shirley, England

3.2.16 Padding machine: Laboratory, Tsujh Dyeing Machine Mfg., Osaka, Japan

3.3 Procedure

3.3.1 Effect of the Pigment/Binder Ratio on Inkjet Ink Properties

Four sets of pigmented inkjet inks with various pigment-to-binder ratios were prepared. The pigment particles were dispersed by the different dispersion technologies as follows: Polyester polymer dispersion was prepared by Dainichiseika Co., in Japan; surfactant dispersion prepared by Fuji Pigment Co., Ltd. in Japan; micro-encapsulation by Dainippon Ink and Chemicals Inc. in Japan, and surface modification by Cabot Co., in USA.

3.3.1.1 Preparation of Pigmented Inkjet Inks

The dispersed pigments, binder, solvent and additive are mixed proportionally to get a uniform ink as shown in Table 3-1. The principal care is to tune the

stable pH range of each material. The pigmented inkjet ink is stable under a pH range of 7 to 10. Each ink mixture was filtered through a very fine nylon mesh screen (400 mesh).

The properties of four types of pigment techniques are shown in the Table 3-2.

Table 3-2: The inkjet ink formulations of water-based dispersion of pigment and polymer at the 1/0.5 pigment/binder ratio.

Pigment Dispersion	Concentration	% solid	Cyan	Magenta	Yellow	Black
NK A-12 binder	0.45	1.75	3.89	3.89	3.89	3.89
Cyan (S-7 C-17)	0.095	3.5	36.84	-	-	-
Magenta (S-7 M-12)	0.097	3.5	-	36.08	-	-
Yellow (S-7 Y-20)	0.097	3.5	-	-	36.08	-
Black (S-7 K-5)	0.101	3.5	-	-	-	34.65
Glycerin	1	5	5	5	5	5
Ethylene glycol	1	10	10	10	10	10
Surfactant	0.1	0.5	5	5	5	5
Water	1	residue	39.27	40.03	40.03	41.46

The ink formulations are different by varying the pigment/binder ratios as 1/0.5, 1/1 and 1/2 (%solid). They are shown in Table 3-3.

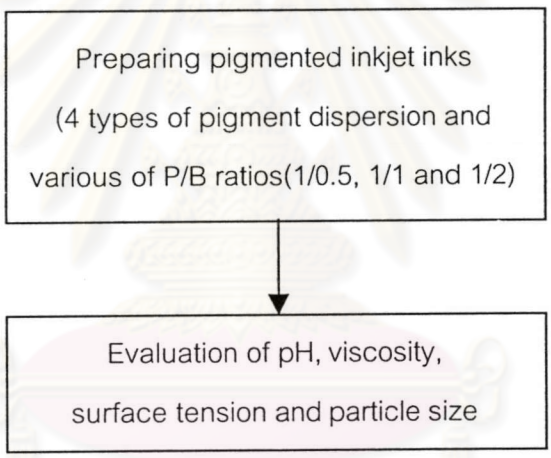
Table 3-3: The pigment and binder concentrations to obtain P/B ratios

P/B ratio	Pigment (%solid)	Binder (%solid)
1/0.5	3.5	1.75
1/1	3.5	3.5
1/2	3.5	7.0

3.3.1.2 Characterization of Pigment Dispersions and Ink Properties

The pH, viscosity, surface tension and particle size of the inks were measured in the present ink formulation for the inkjet printing.

- pH measured by pH meter
- Viscosity measured by Brookfield viscometer
- Surface tension measured by Surface tensiometer
- Particle size measured by Zetasizer and Light scaterring



Flow chart 3.1 Effect of the Pigment/Binder ratio on Inkjet ink properties

3.3.2 Effect of the Pigment/Binder Ratio on Fabric Printing

3.3.2.1 Preparation of Pre-treatment Solution

a. Pre-treatment solution is prepared by adding poly(vinyl alcohol) by weight in the rapidly stirred deionized water. The usual range of the ratio of

poly(vinyl alcohol) to water is 10% by weight. The mixture is stirred for around 10 minutes at room temperature, 10% alumina is prepared by the same way as that of 10% poly (vinyl alcohol). The alumina dispersion is added and the mixture is stirred by a mechanical homoginizer at a constant speed of 8,000 rpm for 30 minutes at room temperature. The volume ratio of 10% poly(vinyl alcohol) to 10% alumina is at around 1:4.

b. The cleaned cotton fabrics were treated with the mixed solution of poly(vinyl alcohol) and alumina at 100% padding. The treated fabrics are dried at room temperature.

3.3.2.2 Printing on the Pre-treatment Fabrics

The pigmented inks were printed on the padded cotton fabrics by EPSON Stylus Color 3000. The printed fabrics are dried in an oven for 10 minutes at 150^{o}C.

3.3.2.3 Evaluation of the Printed Fabrics

The printed fabrics are evaluated for color value, air permeability, bending length and wet/dry crockfastness.

a. Color Measurement

After printing, color values of the printed fabrics: cyan, magenta, yellow, black, red, green and blue were measured by spectrophotometer (X-Rite Digital Swatchbook). The testing condition by Gretag Mecbeth Spectrolino was the measurement geometry $45^{\circ}/ 0^{\circ}$, Illuminants D 65, A/10, D 50. The 2° observer was used based on CIE 1931.

The x and y color values were created as a color gamut (2 dimension) as shown in Figure 3-2. The L*, a* and b* color values were calculated as a color volume. The color volume was calculated by using the color gamut volume program provided by Canon Inc. The method of calculation is shown in Appendix B.

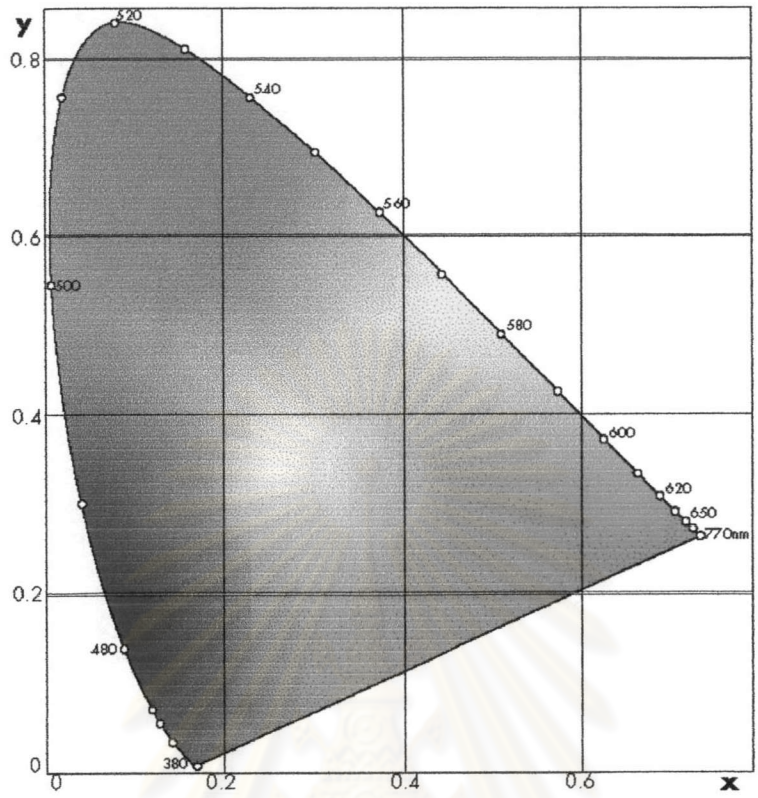


Figure 3-2 The xy color space based on the color matching functions of the Standard Observer.

b. Air permeability

The printed colors on the fabrics: cyan, magenta, yellow, black, red, green and blue were measured for the air permeability using a Shirley air permeability tester. The air permeability of individual specimens was calculated using data read directly from the test instrument in the SI unit as $cm^3/s/cm^2$. The air permeability of the printed fabrics was evaluated based on ASTM D 737-96 test method.

c. Stiffness

A stiffness tester (cantilever test) was used for testing the printed colors of cyan, magenta, yellow, black, red, green and blue. The stiffness of the printed fabrics was measured in the terms of the bending length. The stiffness test method was based on ASTM D1388-96 test method.

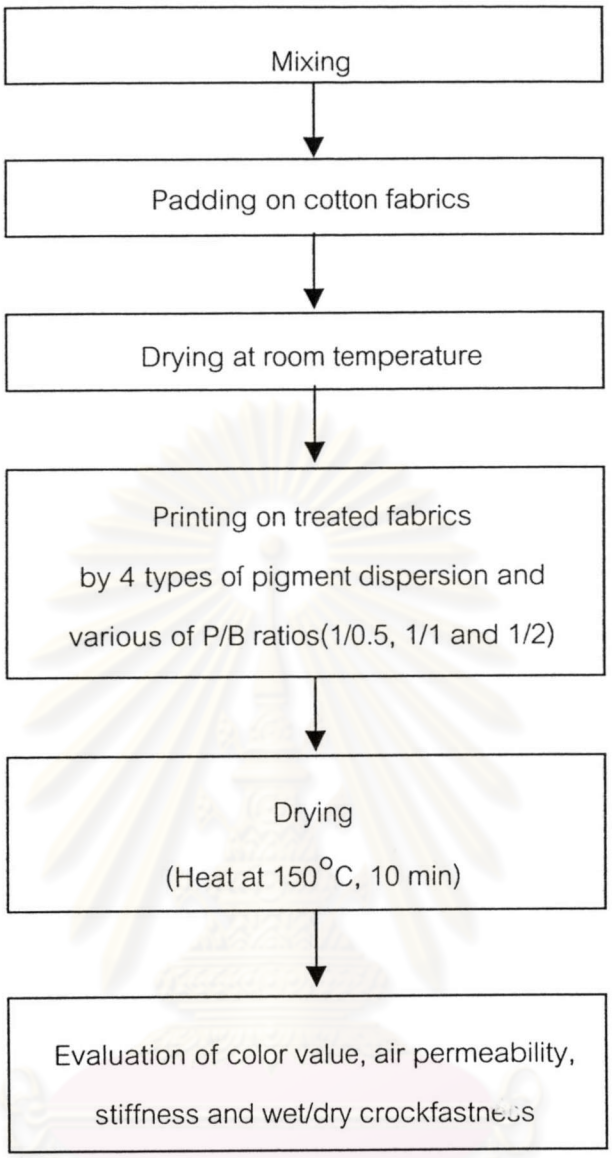
d. Crockfastness

The wet and dry crockfastness of the printed fabrics: cyan, magenta, yellow, black, red, green and blue were measured by AATCC crockmeter. Test procedures employing white test squares, both dry and wet, with water were given. The AATCC crockmeter method was based on AATCC 8-1969 test method.

e. Morphology of Fabrics

All treated fabrics were analyzed for the morphology in terms of size and surface texture by SEM technique.

The depth of ink penetration was observed with cross-sectioned printed fabrics. Cross-sectioned printed fabrics were photographed by Image Analyzer and investigated to characterize the ink absorption of the fabrics.



Flow chart 3.2 Effect of the Pigment/Binder ratio on fabric printing

3.3.3 Effect of Ink Dispersion on the Four Types of Fabric

3.3.3.1 Preparation of Pre-treatment Solution

a. The mixed solution of 10% poly(vinyl alcohol) and 10% alumina were made as those in Section 3.3.2.1

b. 10% Sunfix 555 solution was prepared by adding sunfix 555 in deionized water with a constant stirring rate for 30 minutes at room temperature. The usual range of acrylic sunfix 555-to-water ratio is 10% by weight.

c. 3% poly(ethylene oxide) solution was prepared by adding poly (ethylene oxide) rapidly in the stirred deionized water. The usual range of adding poly (ethylene oxide)-to-water ratio is 3% by weight. The mixture was stirred for around 45 minutes at room temperature.

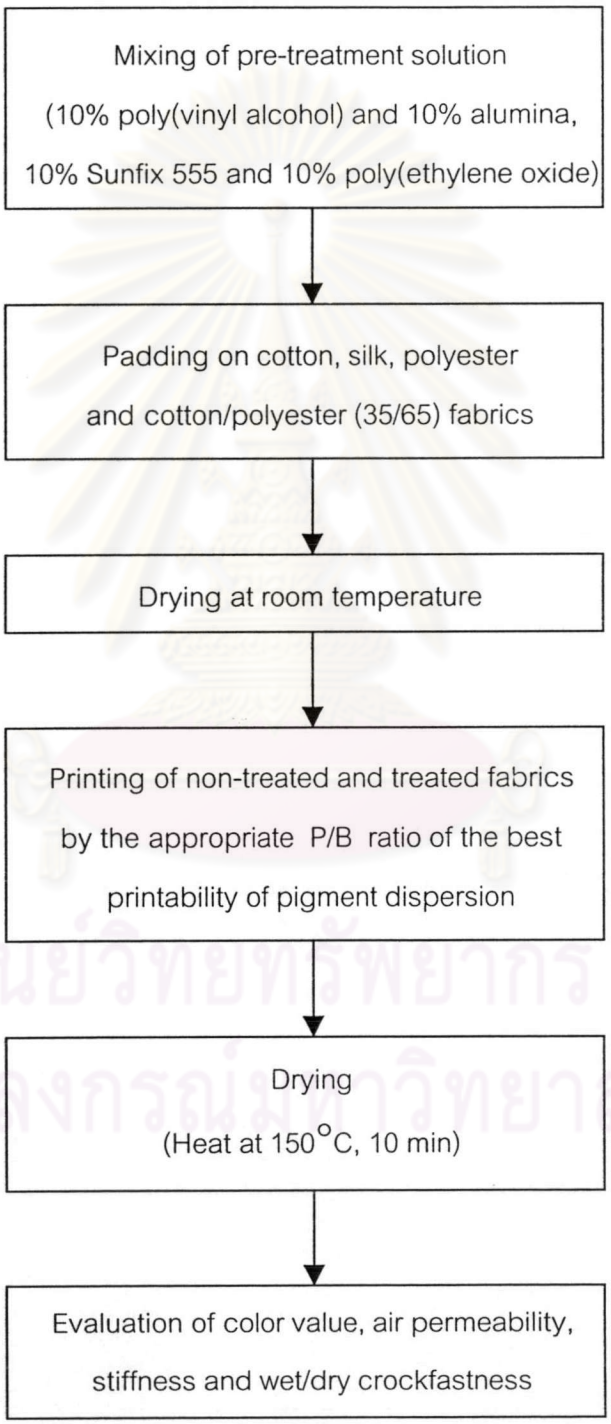
3.3.3.2 Printing on the Pre-treatment and Non-treatment Fabrics

There are four types of fabrics namely cotton, silk, polyester and cotton/polyester (35/65). Each type of the fabric was pre-treated by the mixed solution of 10%w poly(vinyl alcohol) and 10%w alumina, 10%w Sunfix 555, and 10%w poly(ethylene oxide).

The padded fabrics were printed using the appropriate pigment/binder ratio of the best printability of pigment dispersion technique. The pigment/binder ratio, which shows the best result of the printed fabrics in Section 3.3.2 was selected for further use.

3.3.3.3 Evaluation of the Printed Fabrics

Finally, evaluations of the printed fabrics were made as shown in Section 3.3.2.2



Flow chart 3.3 Effect of ink dispersion on the four types of fabric