CHAPTER III

EXPERIMENTAL

3.1 Materials and Chemicals

3.1.1 Pigment dispersion from Mikuni Color Ltd., Himeji, Hyogo, Japan

a. CYAN 11137A: C.I. Pigment Blue 15:3

Specific gravity, 1.4-1.7

Percent volatile by weight, 84.3%

Chemical class: Phthalocyanine

b. MAGENTA 11135A: C.I. Pigment Red 122

Specific gravity, 1.4-1.5

Percent volatile by weight, 79.7%

Chemical class: Quinacridone

c. YELLOW 11138A: C.I. Pigment Yellow 155

Density, 1.4 g/cm^2

Percent volatile by weight, 80%

Chemical class: Diazo

d. BLACK 11136A: C.I. Pigment 7 (Carbon black)

Specific gravity, 1.8-1.85

Percent volatile by weight, 76.8%

Chemical class: Carbon black

3.1.2 Binders

a. BR-700 from Mikuni Color Ltd., Himeji, Hyogo, Japan

Acrylic ester copolymer, aqueous emulsion,

Flash point, 68 °C (open cup)

b. NK VANATEX S-711 from Shin-Nakamura Chemical Co., Tokyo, Japan

Acrylic emulsion, pH 5, non-volatile 48.5%,

Viscosity >1000 mPa s

3.1.3 Other Chemicals

a. Diethylene glycol ($C_4H_{10}O_3$) from Fluka Chemie AG CH-9471 Buchs, Switzerland

Analytical grade, M = 106.12 g mol^{-1}

b. Glycerol ($C_3H_8O_3$) from Merck, Darmstadt, Germany

Analytical grade, M = 92.10 g mol^{-1}

c. Fumed silica (SiO_2) from Degussa A.G., Frankfurt, Germany

Specific surface area, 300 ± 30 m^2 g^{-1}

Average primary particle size, 7 nm

d. Poly(ethylene oxide) from Meisei Chemical Works, Ltd.,

Kyoto, Japan

$\bar{M}_w = 2 \times 10^6 - 3 \times 10^6$ dalton

3.1.4 *Fabric materials*

Scoured cotton fabric: plain weave, construction 140x75, weight 127.28 g m^{-2}

3.2 Apparatus

3.2.1 Epson Stylus 3000 Inkjet Printer, Seiko Epson Corporation, Tokyo, Japan

3.2.2 Cantilever Stiffness Tester: Shirley Developmented Limited, England

3.2.3 Air permeability tester: Shirley, England

3.2.4 Crockmeter: A.A.T.C.C. Crockmeter, ATLAS Electric Device Corporation, USA

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

3.2.6 Viscometer:

a. Brookfield DVIII Programmable Rheometer/ TC500, MA, USA

b. Model: RVT,Spindle and chamber: SC4-14/6R Brookfield, USA

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

3.2.8 Surface tensiometer: K8, Kruss, Germany

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

3.2.10 pH meter: SA 720, Orion Research Incorporated, USA

3.2.11 Padding machine: Tsuji Dyeing Machine Mfg, Osaka, Japan

3.2.12 Particle size analyzer(Zeta Sizer): OTSUKA ELECTRONIC Laser Zeta Potentiometer ELS-8000, Japan

3.2.13 Mechanical stirrer: RE16, IKA-Labortechnix, Germany

3.2.14 Dynamic Mechanical Analyzer (DMA): 7e, Perkin Elmer, USA

3.3 Procedure

3.3.1 Preparation of Fabric

3.3.1.1 Preparation of Nontreated Cotton Fabric

Unfinished cotton fabric was washed with soap, then cleansed with water and dried at ambient atmosphere. The dry cotton fabric was ironed to gain a flat and smooth surface.

3.3.1.2 Preparation of Pretreated Cotton Fabric

The poly(ethylene oxide) was slowly added into deionized water and stirred by a magnetic stirrer at 50 °C until it become a clear solution. The formulation of poly(ethylene oxide) solution was shown as follows:

- Poly(ethylene oxide) concentration: 3 %wt
- Deionized water concentration : 97 %wt

The nontreated cotton fabrics in Section 3.3.1.1 were padded with the pretreatment solution to have a 100 % pick up using a padding machine. The padded cotton fabrics were dried in an oven at 80 °C for 10 minutes.

3.3.1.3 Backing of Fabric

The pretreated cotton fabric in Section 3.3.1.2 was cut into an A4 size. It was taped with a two-sided sticky tape onto a smooth, flat surface, such as a plastic

film as a backing material. The backing material should have a uniform thickness for inkjet printing.

3.3.1.4 Nontreated Cotton Fabric

The nontreated cotton fabric in Section 3.3.1.1 was cut into an A3 size. This size was suitable for screen printing.

3.3.2 Preparation of Aqueous-Based Pigmented Inks

3.3.2.1 Aqueous-Based Pigmented Inkjet Ink

The recipe for the pigmented inkjet ink in this experiment is shown in Table 3-1. The binder-to-pigment ratio was fixed at 2 to 1. Diethylene glycol, glycerine, S-711 binder, and each pigment dispersion were added sequentially in deionized water with continuous agitation. Sodium hydroxide solution was added to the ink to adjust the solution pH to around 9. The ink was then filtered through a filter having 0.5 nm mean pore size. The coarse particles were thus eliminated to prevent clogging of the printed head.

Table 3-1 Recipe for the pigmented inkjet ink

Composition	Concentration (wt %)			
	Cyan	**Magenta**	**Yellow**	**Black**
Pigment (Cyan)	4	-	-	-
Pigment (Magenta)	-	4	-	-
Pigment (Yellow)	-	-	4	-
Pigment (Black)	-	-	-	4
Diethylene glycol	10	10	10	10
Glycerine	15	15	15	15
Binder	16.49	16.49	16.49	16.49
Water	61.61	47.4	54.5	54.5

3.3.2.2 Aqueous-Based Pigmented Screen Ink

The recipe for the pigmented screen ink is shown in Table 3-2. The binder-to-pigment ratio was fixed at 2 to 1. BR-700 binder, fume silica, pigment dispersion, and NK-faster-MEG catalyst were each added while stirring into a glass beaker.

Table 3-2 Recipe for the pigmented screen ink

Composition	Concentration (wt %)			
	Cyan	**Magenta**	**Yellow**	**Black**
Pigment (Cyan)	10	-	-	-
Pigment (Magenta)	-	10	-	-
Pigment (Yellow)	-	-	10	-
Pigment (Black)	-	-	-	10
Binder	20	20	20	20
Fume silica	6.63	4.57	3.13	2.19
Catalyst (NK faster MEG)	0.21	0.21	0.21	0.21
Water	63.22	65.28	66.72	67.66

3.3.3 Printing

3.3.3.1 Inkjet Printing

Cyan, magenta, yellow, and black inks were printed on the padded cotton fabric using a modified Epson printer. The printer was calibrated according to the manufacture instruction. The test forms were applied and printed with Adobe Photoshop program without any color matching function and resolution of 1,440 dpi. To obtain an optical density (the maximum value) of the prints, triple printing at the same area was carried out. After printing, they were dried in an oven at 100-120 °C for 10 minutes.

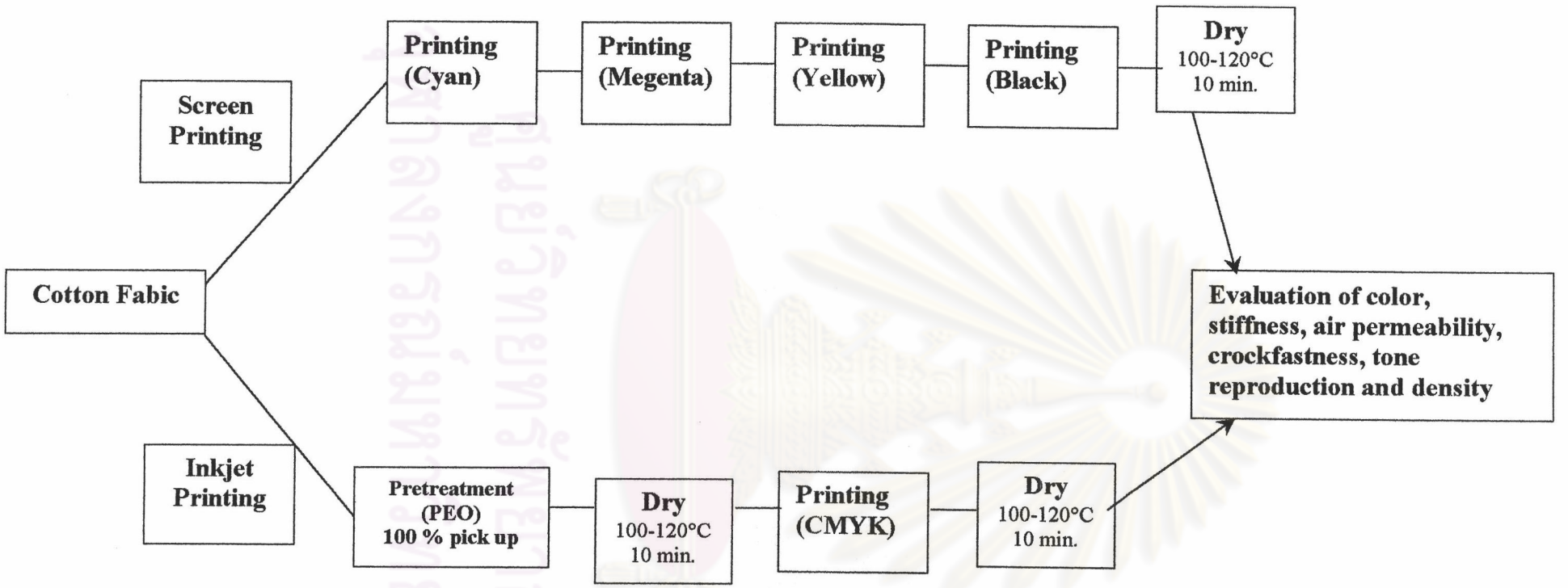

Figure 3-1 Diagram of screen printing and inkjet printing sequences

3.3.3.2 Screen Printing Sequence

The nontreated cotton fabric in Section 3.3.14 was printed by screen printing. The pigmented inks of cyan, magenta, yellow, and black inks were printed sequentially. After printing, they were heated to dry and to fix the ink film at 100-120 °C for 10 minutes.

3.3.4 Characteristics of Binder and Ink

3.3.4.1 Viscosity

The pigmented inkjet inks were measured for their the viscosity, Brookfield DVIII Programmable Rheometer, spindle number 18 at the temperature of 25 ± 0.2 °C with many shear rates. The range of the shear rates was from 50 to 250 rpm.

The viscosity of the pigmented screen inks was measured by Brookfield viscometer (modal RVT, with a small sample adapter and spindle number 14. The measured value at 25 ± 0.2 °C under various rates of 2, 4, 8, 20, and 40 (sec^{-1}) were calculated by multiplying 0.4 to yield viscosity in mN m^{-1}.

3.3.4.2 Surface Tension

The pigmented inkjet inks were measured for their surface tension by a ring method in the K8 surface tensiometer.

3.3.4.3 Particle Size

The pigmented inkjet inks were measured for particle size using the Laser Zeta Potentiometer ELS-8000.

3.3.4.4 Glass Transition Temperature and Young's Modulus of the Binder

The glass transition temperature, Tg and young's modulus of the binder films were measured, by Dynamic Mechanical Analyzer (DMA), to explain the relationship of film property and stiffness of the printed cotton fabric.

3.3.5 Characterization of Printed Cotton Fabric

3.3.5.1 Absorption of Inks on Cotton Fabric by Optical Microscopy

The depth of ink penetration was observed with a cross-section printed cotton fabric using an optical microscope. The depth of ink penetration was photographed, and investigated to characterize the absorption of ink into the cotton fabric.

3.3.5.2 Stiffness

The stiffnesses of the nontreated and pretreated cotton fabric were measured in the terms of the bending length. After printing, the printed colors on the pretreated cotton fabrics: cyan, magenta, yellow, green, blue, red, and black were

measured for the bending length by a stiffness tester (a cantilever type). The stiffness was evaluated based on ASTM D 1388-96 test method.

3.3.5.3 Crockfastness of the Printed Cotton Fabric

The crockmeter was used for testing the printed colors of cyan, magenta, yellow, green, blue, red, and black on the cotton fabric. The crockfastness test method was based on AATCC 8-1969 test method.

3.3.5.4 Air permeability

The nontreated, pretreated, and printed cotton fabric were measured for air permeability by an air permeability tester. The air permeability of individual specimens was calculated using the data read directly from the test instrument in the SI unit as cm^3 s^{-1} cm^{-2}. The air permeability test method was based on ASTM D 737-96 test method.

3.3.5.5 Surface Morphology of Cotton Fabric

Surface morphology of cotton fabric was sighted and photographed by scanning electron microscopic technique (Joel JSM-6400).

3.3.5.6 Color Measurement

Color values of the printed cotton fabric: cyan, magenta, yellow, green, blue, red, and black were measured by a spectrophotometer (Gretag Macbeth Spectrolino). The Gretag Macbeth Spectrolino has a measurement geometry 45°/0°,

by illuminants D65. The 2° observer was used based on CIE 1931. The color value was measured in terms of CIE-L*a*b* and xyz color space.

The x and y color value were created as a color gamut (2 dimension) as shown in Figure 3-2. The L*, a* and b* were calculated to give a color volume. The color volume was calculated using the color gamut volume program provided by Canon Inc.[23]

Furthermore, The u' and v' color value were calculated to yield the color saturation, S_{uv}, from the following equation:[23]

$$S_{uv} = 13\ ((u'-u'_n)^2 + (v'-v'_n)^2)^{1/2} \qquad (3.1)$$

where

u'_n, v'_n are the values of u', v' for the reference white

u', v' are the u', v' diagram, which is calculated from x, y color values as follows:

$$u' = 4x/(-2x+12y+3) \qquad (3.2)$$

$$v' = 9y/(-2x+12y+3) \qquad (3.3)$$

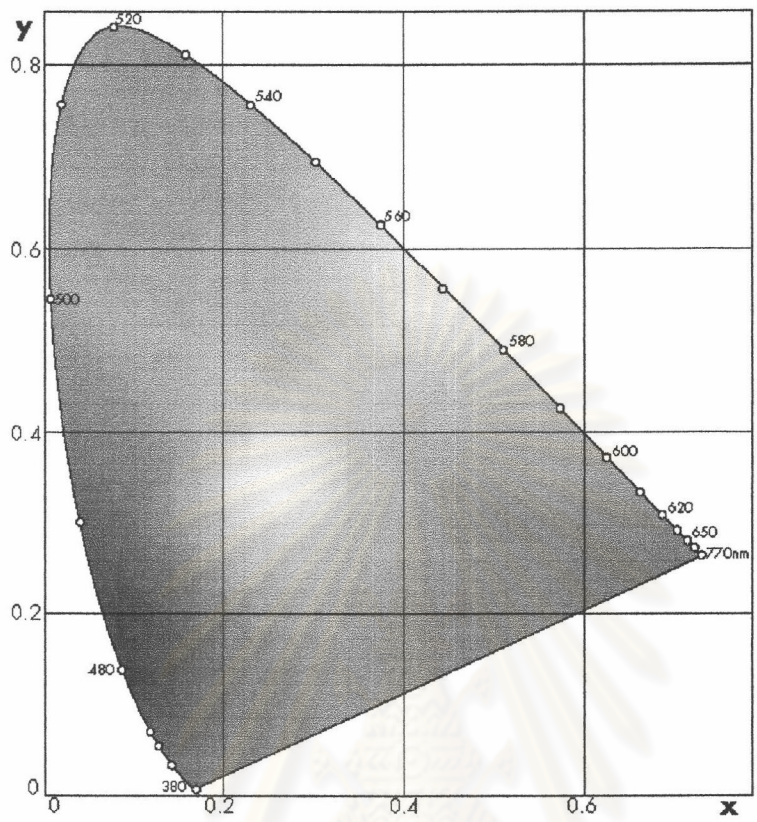

Figure 3-2 The xy color space based on the color matching function of the standard observer.