Pigmented Inkjet Ink Dispersion for Silk Fabric Printing

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Abstract

This research concerns the study of the effects of pigmented inkjet dispersion for use on silk fabric. The pigmented inkjet inks were formulated using two types of pigment dispersion techniques: surface modification and micro-encapsulation. Properties of both inks are: viscosity 3.5-5 mPa s, surface tension 38-45 mN m^{-1}, and particle size 0.22-0.23 µm. The stability of the inks was examined for changes in viscosity and particle size distribution. The inks were stored at ambient room temperatures for 12 weeks. After storage, the inks viscosity was increased by 20-40% and the particle size by 2-15%. The printed silk fabric was analyzed here only for tone reproduction and color. The surface modified pigmented inks yielded high optical density, good tone reproduction, better color gamut, and gamut volume. This research explains the influences to cause such results.

Introduction

Micro-encapsulation is one of the pigment dispersion techniques normally used in preparing inkjet inks. The micro-encapsulated pigments have a thick acrylic polymer layer with self-dispersion ability on pigment surfaces. The dispersions are excellent in dispersability and stability. The other technique for pigment dispersion is the pigment surface modification technique. It is the technique related to chemical bonding and the number of functional groups of the surface of the pigment. This technique leads to well characterized pure pigments, void of free polymers and impurities. It was found that the inks show excellent print qualities.

In this research, two types of pigment dispersion will be used for preparing the pigmented inks. Additional studies on pigment dispersion efficiency between the micro-encapsulation technique and the surface modification technique in terms of viscosity, surface tension and particle size are carried out. The inks will be printed on silk fabric by an inkjet printer. After printing, comparison of the print quality in terms of optical density, color gamut and tone reproduction between two sets of the pigmented ink will be elucidated.

Procedure

Preparation of Non-treated and Treated Fabrics

Silk fabric (plain weave, 82×85, 104 g m^{-1}) was washed with soap then rinsed with clean water and dried at ambient atmosphere. The fabric was ironed for a smooth surface. Silk fabric was treated using 10% Sanfix 655 (cationic acrylate polymer, Sanyo, Kyoto, Japan) and 10% urea solution as a pretreatment agent. The silk fabric was padded by a padding machine (Tsuji Dyeing Machine, Mfg, Osaka, Japan) with 100% pick up and then dried in an oven (Rapid Labortex Corp., Taiwan) at 80°C for 10 minutes. In order to print textile substrates, it is necessary to assure fabric stability in the printer feed rollers. Deformation of the fabric was prevented by placing six strips of masking tape on the fabric back with a flat plastic film having uniform thickness for better ink reception.

Preparation of Pigmented Inkjet Inks

The inkjet inks were prepared by varying the dispersed pigment, either obtained by the micro-encapsulation technique or the surface modification technique with a ratio of pigment to binder of 1 to 2. The formulation for the pigmented inkjet ink is shown in Table 1.

The ink components were mixed together, in which the dispersed pigment was used as a colorant, a S-711 polymer resin (Shin Nakamura, Japan) as a vehicle or binder, the deionized water as a main solvent, diethylene glycol, glycerol and urea as a co-solvent. The mixture was then stirred until a homogeneous solution was obtained. Then, sodium hydroxide (10% by weight) was added to control the ink pH to a range of 7-9. The inks were later filtered through 5-µm pore filtering paper for preventing clogging problems.

Table 1. Fomulation of Pigmented Inkjet Inks

Composition	Concentration (%wt)
Pigment dispersion	4.0
Diethylene glycol	10.0
Glycerol	10.0
Urea	5.0
Binder (S-711)	8.0
De-ionized water	63.0
Total	100.0

Physical properties of two sets of dispersed pigments of cyan, magenta, yellow, and black are shown in Table 2. After the inks were dispersed, they were stored in a desiccator, which was connected to a suction pump for eliminating air bubbles. Then the four colors of inkjet ink were each loaded into an inking unit of the printer (Epson Stylus Color 3000, Seiko Epson Corp., Tokyo, Japan).

Characterization of the Materials

The pigmented inkjet inks were evaluated for the ink properties in terms of viscosity, surface tension, particle size distribution, content of dispersing agents and glass transition temperature of the polymeric binder. The pigmented inkjet inks were measured for their viscosity using a Brookfield viscometer model DVIII (Stoughton, U.S.A.). The inks were filled into a sample holder of the equipment and then measured at the temperature of 25°C by various shear rates. The shear rates under study were between 50 to 250 rpm. The surface tensions of the inks were evaluated using a ring method in K8 surface tensiometer (Hamburg, Germany). A small amount of dispersed pigments and pigmented inkjet inks was suspended and fed into the input channel of the equipment for measuring their particle sizes. The information of particle size distribution was taken from Malvern laser scattering analyzer model Mastersizer S long bed Ver. 2.11 (United Kingdom). The micro-encapsulated pigments were evaluated for the glass transition temperature, T_g, of the polymer binder S-711 by NETZSCH DSC200 Thermische Analyse (Bayern, Germany).

Characterization of the Printed Fabrics

The printed fabrics were evaluated for the print qualities. The printing qualities were measured in terms of color of the printed fabrics. Cyan, magenta, yellow, black, red, green and blue were measured in terms of density and color values in tristimulus value and CIELAB color space using a spectrophotometer (model spectrolino), measurement geometry 45°/0°, illuminants D65, CIE 1931 2° observer. The tristi- mulus values (X, Y, Z) were transformed to chromaticity coordinates (x, y, z) for creating a color gamut (2 dimensions). The L^*, a^* and b^* color values were used to calculate a color volume. The color volume was calculated using the color gamut volume program provided by Canon Inc., and chroma, the c^*_{ab}, was calculated from a^* and b^*.[1] Microdensitometer (PDM-7, Konica, Tokyo, Japan) was used to measure the microdensities of the small areas and fiber.

Results and Discussion

The Characteristics of Pigmented Inkjet Inks

Two types of pigment dispersion for four color pigments used are shown in Table 2.[2] The physical properties of pigment dispersions used in this research for preparation of the inkjet inks are also given in Table 2. The two types of pigment dispersion have a different functional group. The surface modification technique using sulfonic groups to modify the surface of pigment particle, whereas the micro-encapsulation technique used the encapsulated polymer embracing pigment particles.[3,4] The ratios the pigment to polymer (by weight) for PB 15:4, PR 122, PY 128 and PBk 7 are 1:0.54, 1:0.52, 1:3.24, 1:0.41, respectively. The polymer binder used in this research is polyacrylate emulsion. The mean diameter of the parti- cles of the emulsion is of approximately 0.24 µm. The properties of the binder S-711 are shown in Table 3. The required properties of inkjet inks are of excellent stability, high brilliance, low viscosity, high surface tension, long shelf life, and rapid drying time. When examining the rigors of the process, droplets are heated only for microseconds to reach 300-500°C in a print head and the droplets are then ejected through the nozzles of 20-100 µm diameter.[5] The inkjet ink properties used in this research conform to the above mentioned characteristics.

Table 2. The Physical Properties of Four Color Pigments

Dispersion technique	Color	Properties			
		Pigment concentration (%)	pH	Particle size (µm)	Viscosity (mPa s)
Surface modification	Cyan (PB15:4)	10.4	8.09	0.24	1.55
	Magenta (PR122)	10.2	7.94	0.25	1.86
	Yellow (PY 74)	9.8	8.15	0.30	1.83
	Black (PBk 7)	19.6	7.60	0.24	3.23
Micro-encapsulation	Cyan (PB15:4)	14.3	8.64	0.23	3.74
	Magenta (PR 122)	14.4	8.76	0.23	4.84
	Yellow (PY128)	16.7	9.43	0.23	8.46
	Black (PBk 7)	14.3	8.48	0.22	3.12

Table 3. Characteristics of the S-711 Binder

Properties	Amount
Nonvolatile (%)	48.5
Viscosity (mPa s)	1000-1500
pH of dispersion	5
Surfactant type	nonionic
T_g (°C)	1.2

Viscosity of Pigmented Inkjet Inks

Print performance comes from how the inks generate images on the substrate with the specific properties within a designed range. To eject droplets correctly and to get enough density, inkjet ink must have the proper physical and optical properties (low viscosity and high surface tension). The ink formulation was kept constant at a pigment-to-binder ratio of 1:2 by weight based on total weight of the ink. The viscosity of the inkjet inks was measured at 25°C with a spindle #18 and shear rate at 250 s^{-1}. The viscosity of the inks made from surface modified pigments of cyan, magenta, yellow and black inks was found 3.58, 3.85, 3.58 and 3.55 mPa s, respectively. The inks made from micro-encapsulated pigments have the viscosity of 4.45, 4.71, 4.81 and 4.27 mPa s. The ink made from micro-encapsulated pigments, therefore gave the higher viscosity than those from the surface modified pigments because of the extra concentration of the polyacrylate emulsion used for encapsulating the former pigment dispersion. Basically, the inkjet inks are colloidal suspension; they should exhibit a significant shear thinning behavior, which this is expected to impact upon the particle distribution across the nozzle capillary leading to a jet. The shear thinning behavior disturbs the flow of inkjet ink because the inkjet ink system should be of the Newtonian fluid, which maintains a constant viscosity regardless of shear rate. The two pigmented inkjet inks in this research perform somewhat like a non-Newtonian fluid, which might be caused by the other components in the ink ingredient. However, when we ignore the low shear region (66 s^{-1}), other shear rates seem to give the relatively constant viscosity since the differences between each shear rate is not significant. The high viscosity at low shear region could possibly be resulted from the buildup of structure between pigment and polymer binder.

Surface Tension of Pigmented Inkjet Inks

Surface tension helps control the meniscus at the nozzle. A high surface tension is desirable for pigmented inkjet ink on a uniform and stable drop formation on the nozzles. The surface tension of the ink has to be lower than the surface energy of the fiber of the fabrics. Surface modified pigments for Cyan, magenta, yellow, and black inks give similar surface tension of 45, 45, 45, and 41 mN m^{-1}, respectively, whereas the micro-encapsulated pigmented ink provides 38, 39, 41, and 40 mN m^{-1} for cyan, magenta, yellow and black inks, respectively. The surface tension of surface modified pigmented inks is higher than micro-encapsulated pigmented inks. As a result of surface tension, regularity of droplet formation and pigment loading are possibly critical to textile inkjet print quality.

Particle Size

The particle size was measured using dynamic light scattering method from Malvern laser scattering analyzer. The mean particle size of the cyan, magenta, yellow and black inks were very similar at around 0.22 µm to 0.23 µm for both inks made from surface modified pigments and micro-encapsulated pigments. The clogging problem of the ink was not found during printing. The nozzles provide very good jetting, because the opening of the nozzles may vary from about 40 µm to about 100 µm.[4]

Stability of Pigmented Inkjet Inks

The pigmented inkjet inks were stored at room condition for 12 weeks in a stability study of the inks. The changes of viscosity after 12 week storage are insignificant for both surface modified and micro-encapsulated pigmented inks. The required properties of inkjet inks of excellent stability, high brilliance, low viscosity, high surface tension, long shelf life, and rapid drying time could be thus fulfilled. Stabilization of the dissociated state can be achieved by controlling the salts and ions added. These factors affect the size of the hydrostatic and electrostatic radii of the particles in the vehicle. The micro-encapsulated pigment contains the carboxylate group (COO^-) while the surface modified pigment has the sulfonate group (SO_3^-) on the modified surface. A better stability was observed in the surface modified pigmented inks than those of micro-encapsulated pigmented inks. The viscosity of the inks made from micro-encapsulated pigments increases somewhat greater than those from surface modified pigments. Runability of pigmented inkjet ink relies on various ink properties such as anti-kogation, heat stability, and anti-clogging performances. Especially anti-clogging property is thought to be the most serious problem of emulsion-based ink. Fortunately, by introducing several kinds of hydrogen bonding functional groups to polymer molecules, which can have mutual interaction with humectants, the ink could then be stabilized well under the dry condition. In this research, urea was added in the ink formulation for reducing the clogging problem.

The particle size distributions of the initial inks were compared with the particle size distribution after storage for 12 weeks. The inks made from the surface modified dispersion technique of cyan, magenta and black inks show a little change in size distribution except that of yellow ink. The particle size distribution of the inks made from microencapsulated pigment dispersion was almost constant for every ink color for 12 weeks. It is possible to state that the micro-encapsulated pigments are protected individually from coalescence by the encapsulating polymer. Therefore, the polymer shell behaves like a protective repulsion layer to keep each individual encapsulated pigment apart. Therefore, the particle size distribution before and after storage was the same, no changes were observed.

The Qualities of Printed Silk Fabrics

The pigment-resin printing forms a film when dried, which encloses the pigments and adheres to the fabric. Textile apparel has strict requirements on hand and color fastness. The silk fabrics were printed by a commercial desktop inkjet printer. Normally, the qualities of printed fabrics were analyzed in four categories: 1) appearance-related issues including optical density and tone reproduction; 2) color-related issues including color gamut, chroma, and color gamut volume; 3) permanence issues including crock fastness, wash fastness and light fastness; 4) usability issues including the presence of defects and hand, air permeability, and bending stiffness. For the present work, only tone reproduction and color shall be investigated.

Effect of Pigment Dispersion on Optical Density

Optical density and tone reproduction were evaluated for the visual qualities of the printed fabrics. The original digital pattern consisting of a solid tone pattern and gray levels were printed onto the silk fabric. The optical density of the non-treated and treated silk fabrics measured is shown in Table 4.

The cyan, magenta and black color inks made from the two different pigment dispersions contain the same chemical class of pigment (Table 2). The optical density of the inks made from the surface modified pigments is higher than the inks made from the micro-encapsulated pigments. The difference in optical density between the two sets of ink depends on the illuminant and reflectance through the pigment particles in the ink layer. The micro-encapsulated pigment and surface modified pigment have different weights of polymer concentration, of course they have the same weight of dispersion while making inks but the micro-encapsulated pigment dispersion has a lot more of the polymer in the non-volatile part so they are of higher polymer quantity. The pigment-to-polymer ratio of the micro-encapsulated pigments is also mentioned above. The different weight % of pigment does not give the same tint strength on the pretreated surface. Moreover, the structure of fiber imparts a strong influence on the scattering of light, when measuring the optical density of the silk fabric; the dependence of angle of reflection light is affected by the surface texture of fixed ink layer. The difference in surface tension affects the depth of penetration in fabrics, because low surface tension ink penetrates deeper into the silk fiber and thus gives the lower ink holdout to result in the lower optical density. The ink penetration of micro-encapsulated pigmented ink with a low surface tension is greater than the surface modified pigmented ink.

The micro-encapsulated pigment has a thick layer of polymer shell enclosing pigment particles as a core, while the surface modified pigment by chains of a surfactant is thinner. On the optical density measurement, the illuminating light from a spectrophotometer striking on the encapsulated pigments scattered and reflected internally. The reflected light collected at the spectrophotometer becomes less to give a lower ink density. On the other hand, if the light reflected from the pigment surface is fully collected by the spectrophotometer, it shall then give a higher ink density. Macroscopically, the micro-encapsulated pigments reduce scattering of light in a fixed ink layer and should give higher ink densities. In this context, the advantageous property can be observed in comparison to the ink layers of surface modified pigments; unfortunately, the densities of the micro-encapsulated pigmented ink are lower. As mentioned previously in procedure section, the microdensitometer was used for evaluation of densities of the small printed areas including fiber surfaces. The microdensities of the micro-encapsulated pigmented inks [1.18 (Cyan), 0.85 (Magenta), 0.27 (Yellow)] are higher than those the surface modified pigmented inks [0.87 (Cyan), 0.7 (Magenta), 0.24 (Yellow)].

Effect of Pigment Dispersion on Tone Reproduction

The halftone pattern consisting of percent dot areas from 7 percent (highlight) to 100 percent or solid tone is printed onto the silk fabric. The densities of printed halftone dots on the printed fabric were measured for optical density and expressed in terms of tone reproduction. The tone reproduction of inkjet ink printed silk fabric is illustrated in terms of optical density versus percentage dot area. We observed that the tone reproduction of the inks made from the surface modified pigments is relatively higher than that of the micro-encapsulated pigments.

Table 4. Optical Density on the Non- Treated and Pretreated Fabrics

Color	Surface modified pigmented ink		Micro-encapsulated pigmented ink	
	Non-treated silk fabric	Pretreated silk fabric	Non-treated silk fabric	Pretreated silk fabric
Cyan	1.29	1.45	1.20	1.36
Magenta	1.30	1.46	1.10	1.35
Yellow	1.43	1.52	1.14	1.34
Black	1.40	1.45	1.27	1.31

Effect of Pigment Dispersion on Color and Color Gamut

The gamut performance of different inkjet inks set on the printed silk fabrics was investigated. The influence of different dispersion techniques of the inks is compared. Gamut variation is caused by the different colorants in the inks. The colors on the printed silk fabrics were measured by CIELAB and CIEXYZ systems for evaluating the color strength of different dispersion technologies. It is well known that the pigmented ink inherents inferior properties in color gamut and strength. Comparison between different pigment dispersion techniques, one can see that cyan, magenta, and black pigments by both techniques have the same shade, but the surface modified yellow pigment is yellowish and the micro-encapsulated yellow pigment is greenish. The surface modified pigmented ink gives a larger color space in the x, y chromaticity diagram of the non-treated silk fabric with a larger gamut volume than those of the micro-encapsulated pigmented ink. Penetration of a liquid flowing under its own capillary pressure in a horizontal capillary is described by the Lucas-Washburn equation.[6] This equation shows that the high surface tension ink is infiltrated in the fabric slowly, so the ink is held more on the top of the fabric. The more ink holdout, the higher the ink color gamut is found. The higher surface tension of the surface modified pigmented inks produces the larger color gamut than the micro-encapsulated pigmented ink. The gamut volumes of the two ink sets on the non-treated silk fabric are listed as follows: 7043 and 8475 for surface modified pigmented ink on the non-treated and treated silk fabrics while 5337 and 7933 are for micro-encapsulated pigmented ink on the non-treated and treated silk fabrics. The larger gamut volume is presented by the surface modified pigment ink set than the other set. It is common to consider the three relevant attributes of perception of color as hue and chroma, (or saturation) are the colorfulness or richness of the color, and lightness, which refers to the amount of reflected light. These three attributes are described using the concept of color space, which shows a relationship of colors to one another and which illustrates the three dimensional nature of color.

Conclusions

This article investigates the effect of two types of pigment dispersion techniques for silk fabric printing. Micro-encapsulated pigment dispersion and surface modified pigment are used for the preparation of inkjet ink, which were used later for silk fabric printing. Both inks have their own characteristic because of different pigment environments. The surface modified pigmented inkjet ink gives somewhat better color reproduction on both treated and non-treated fabrics. Likewise, the color gamut of the micro-encapsulated pigmented inkjet ink provides the smaller color gamut on both non-treated and treated fabrics. Plausible explanations concerning the findings are given.

Acknowledgements

This project is supported by Thailand-Japan Technological Transfer Project under Research Profile 21 Imaging Technology, Faculty of Science, Chula- longkorn University. Many thanks for material supporting companies mentioned in the text.

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Biography

Dr. Suda Kiatkamjornwong is currently a full professor (PC 11) at the Department of Imaging and Printing Technology, Faculty of Science, Chulalongkorn University. She also serves as a Vice Dean of Research Affairs at the same faculty. She graduated with a B.Sc. and M. Sc. in Chemistry from the Faculty of Science, Chulalongkorn University, and a Ph.D. in Polymer Science and Engineering from Lehigh University, U.S.A. Her research interests are in the areas of printing materials, and the synthesis of polymers for printing. She also carries out research in super-absorbent polymer and imbiber beads for environmental applications.