https://doi.org/10.2352/ISSN.2169-4451.2019.35.168

Lightfastness of Invisible UV Fluorescent Inkjet Printing on Anticounterfeit Document

Juntira Komasatitaya; Department of Printing and Packaging Technology, Faculty of Industrial Education and Technology, King Mongkut's University of Technology Thonburi (KMUTT); Bangkok, Thailand.

Abstract

This work had an objective to study on lightfastness property of invisible UV fluorescent inkjet printing by comparison between two formulations of inkjet inks onto 2 different basis weight of plain papers using a desktop inkjet printer. The print was invisible under white light, but be visible under UVA/ blacklight. The fluorescent inkjet prints were studied their lightfastness property by exposing of blacklight for 248 hrs. The tested prints were evaluated ink fading. It was found that there was effect of ink fading on the different types of the printed papers which the heavier weight paper type had better lightfastness than that of the lower weight paper type. Furthermore, plastic film lamination on the print had capability to protect the printed from fading.

Introduction

Digital printing technology is currently employed in security printing to protect from counterfeiting, duplication, etc. There are many of innovative digital printing technology that enables the use of a number of security options such as fluorescent inks, clear inks, MICR printing, micro printing, and so on. Inkjet printing is a printing system that convenient to adopt in many applications including of ant counterfeit printing. [1,2,3] The use of fluorescent agent for security purpose has been reported. [4-10]

Fluorescent brightening agent is a colorless organic compound that can stimulate fluorescence under ultraviolet light. It absorbs the ultraviolet in 330 to 360 nm wavelength with the reflected light being at a blue/violet light of wavelength of 400 to 440 nm. Fluorescent brightening agent mostly used in textile whitening; recently in field of paper, and plastic, etc. Its chromophor had at least four conjugated double bonds, which was divided into four groups: stilbene, coumarin, azole, and naphthalimide,that differently suited for different types of materials. Stilbene type, or stilbene derivative (1,2-diphenylethylene) is mainly used for cellulosic fibers such as cotton, whereas the other types are suitable for protein fibers, polyamide, polyester, or synthetic fibers.[11-14] A proper ink for inkjet printing machine had some key properties of low viscosity, proper surface tension, good stability, and high purity for yielding full ejection through tiny nozzles, no clogging, provides full color on printing.[15,16,17,18]

This research continuously focused on UV fluorescent inkjet ink composed of fluorescence dye or pigment for invisible security printing, which detected an ink mark by blacklight, in a range of UVA wavelength. Challenge of using dye in the ink formulation was continuously fading under light for a period of time. The different substrate such as printing paper was important on lightfastness property of the printed image depending on both physical and chemical conditions. This paper was studying on lightfastness of the invisible inkjet inks composed of fluorescent dyes on effect of different printing papers. Methodology was as following: ink preparation, inkjet printing on paper substrate, and lightfastness testing including measurement of reflectance spectrum, and visual evaluation on print samples.

Experimental

Inkjet Ink Formulation

Commercially available fluorescent dyes received from two different manufacturers, which these dyes were industrially used as an optical brightener. The dyes were water soluble and used as received. Dye 1 was stilbene derivative chemical, anionic, pH 9.0±1, good-very good stability in acid-base solution. Dye 2 was unknown. A nonionic alcohol ethoxylate, HLB 12, Sigma Aldrich was used as a surfactant, and an analytical grade ethylene glycol was used as received in inkjet ink formulations. Formulation of the ink prepared in this study was as shown in Table 1, Ink 1 and Ink 2 were made from dye 1 and 2, respectively. These prepared inks should be adjusted to have a suitable property of inkjet: pH~8, viscosity ~3 mPa·s, and 30~50 mN/m of surface tension.

Table 1 Inkjet ink formulations: Ink 1 and Ink 2

Ingredients	Amount (%wt of total ink weight)
Fluorescent dyes: dye 1, or dye 2	7-10
Alcohol ethoxylate surfactant	1.5
Ethylene glycol as a humectant	10-30
Purified water	Residue

Printing and Testing

Invisible Inkjet Printing and Lightfastness Testing

The aqueous based inkjet inks formulated with the fluorescent dye: dye A and dye B was ejected through piezo printhead of a commercial DOD small inkjet printer with a maximum print resolution of 5760 x 1440 dpi. Printing paper substrate was commercial uncoated white plain paper for home and office using: grammages 80 and 100 g/m^2. Paper whiteness was measured in values of CIE L*a*b* as shown in Table 2. After printing step, the printed papers were tested for lightfastness by UVA exposure for 248 hrs. using a blacklight lamp, 360 W, with a dimension of 1200mm x 200∅mm. In addition, some sheets of the printed papers were brought to do dry lamination with polyethylene plastic film on both side of the paper sheet to study effect on visibility and lightfastness.

Measurement and Evaluation on Prints

Reflectance Spectrum

Reflectance spectrums between wavelength 360-700 nm were measured onto the print samples via UV-VIS spectrophotometer, Datacolor 650^{TM} by mean of both UV-exclude and UV-include modes to find the reflectance of the invisible image printed from the UV fluorescent ink. Range of wavelengths and peak of the reflectance spectrum were successively measured.

Table 2 Color values measured using X-rite, SpectroEye

Paper samples (g/m^2)	L*	a*	b*
80	99.82	-0.09	-0.66
100	98.62	-0.09	0.83

Visual evaluation

Smallest font size and minimum line width printed with the invisible inks onto the paper substrates were evaluated by visibility testing under a blacklight lamp; it was done by reading on letters and numbers in sizes varied from 6-26 point, and line width varied from 0.01-2.40 point. In addition, %screen and solid tone (10-100%screen at 10% screen interval) for print tone reproduction was tested for visibility as well. This visual test was statically evaluated the values with arithmetic mode, that was most frequent value, from n=50 persons.

Results and Discussion

Inkjet Ink Formulation

The invisible security inkjet inks made from the UV fluorescent dyes had the physical property as shown in Table 3, which was suitable for DOD inkjet printing. The surface tension 34-35 mN/m were the values that the ink had capable to wet and spread onto the paper surface. pH value that was not damage printhead and nozzle of the printer; ink viscosity that was very low and being as non-Newtonian flow.

Table 3 Physical property of the inkjet ink

Properties	Value/Unit
pH	7.6-7.8
Surface tension#	34-35 mN/m
Viscosity±	2-3 mPa·s

Tensiometer by ring method, ± Brookfield viscometer

Reflectance Spectrum of Invisible UV Fluorescent Inkjet Inks Printing on Paper

Ink 1 composed of the fluorescent dye 1 showed reflected blue light from invisible print-image when stimulated by mean of blacklight lamp. Figure 1-4 showed a reflectance peak at wavelength of 440 nm, and being higher on UV-include stimulation nearly 30 of % increments. The 100 gsm printing paper having yellowish white (see Table 2) apparently showed a peak of reflectance higher than that of 80 gsm paper. That made the reflected blue light on the 100 gsm paper was clearly readable better than that on the 80 gsm printing paper. Figure 3 and 4 showed the spectrum of ink 2 that looked nearly similar to that of ink 1, so dye 2 might be stilbene derivative type.

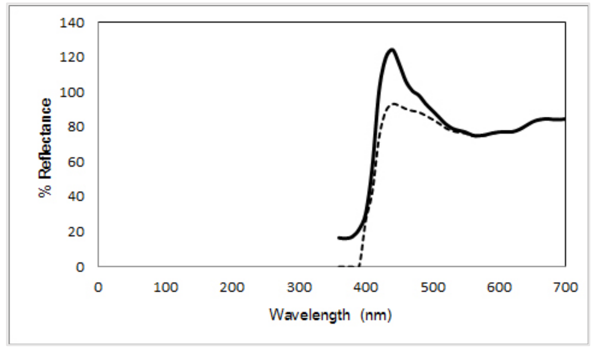

Figure 1 Reflectance spectrum of the fluorescent inkjet ink 1 printed on plain papers measured with UV-exclude (- - -) and UV-include (—) modes: 100 g/m² paper

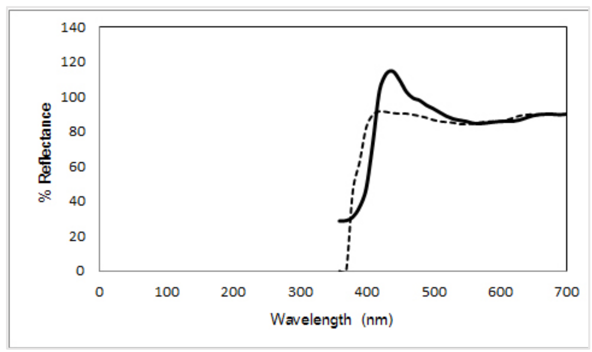

Figure 2 Reflectance spectrum of the fluorescent inkjet ink 1 printed on plain papers measured with UV-exclude (- - -) and UV-include (—) modes: 80 g/m² paper

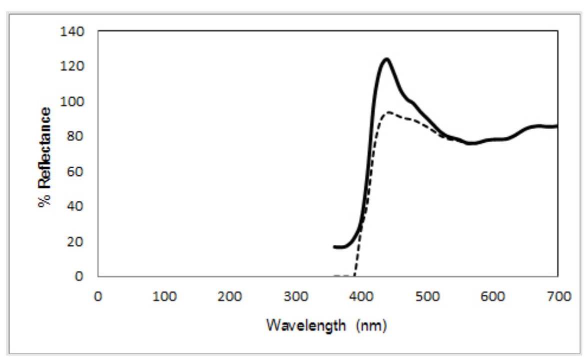

Figure 3 Reflectance spectrum of the fluorescent inkjet ink 2 printed on plain papers measured with UV-exclude (- - -) and UV-include (—) modes: 100 g/m² paper

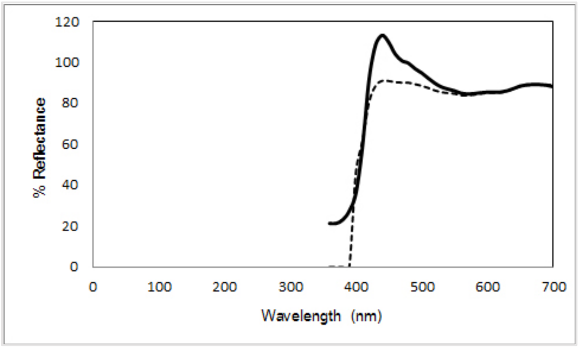

Figure 4 *Reflectance spectrum of the fluorescent inkjet ink 2 printed on plain papers measured with UV-exclude (- - -) and UV-include (—) modes: 80 g/m² paper*

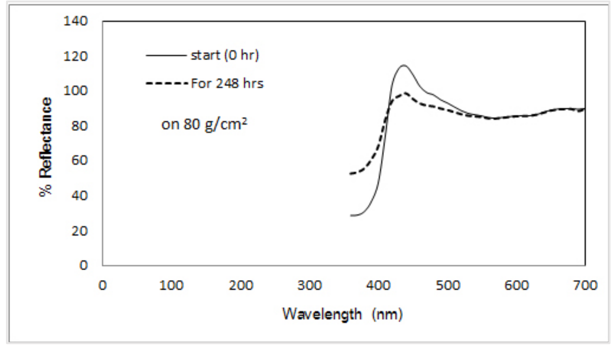

Figure 6 *Reflectance spectrum of the fluorescent inkjet ink 1 printed on plain papers of 80 g/m² before and after exposure by UVA-blacklight for 248 hrs ; measured with UV - include mode*

Lightfastness: Fading of Invisible UV Fluorescent Inkjet Inks Printing on Paper

Reflectance Spectrum

Both ink 1 and ink 2 had fading character as shown in Figure 5-8,that was the inks had fading after exposing by blacklight UVA for 248 hrs with showing of lower peak than the spectrum of early light exposing (0hr). The printing paper was a factor to effect on fading of the ink 1 and 2; 80 gsm paper gave lightfasness lower than 100 gsm paper that was almost 20% reflectance. It might be that, by comparing to the lighter weight paper, the heavier weight paper having more of fibers so it absorbed more of aqueous ink including molecules of the fluorescent dye resulted in slower fading than that of the lighter weight paper. Beside of paper grammage, chemical property of paper and fiber might have influence on ink fading on paper.

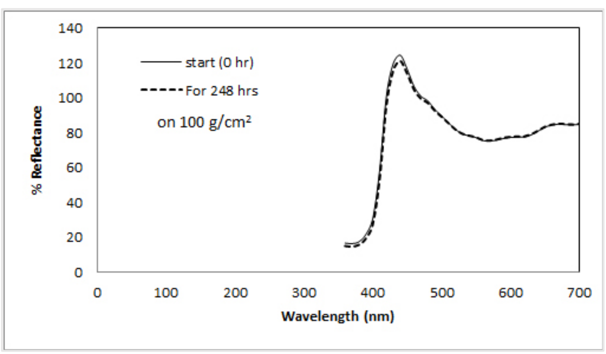

Figure 5 *Reflectance spectrum of the fluorescent inkjet ink 1 printed on plain papers of 100 g/m² before and after exposure by UVA-blacklight for 248 hrs ; measured with UV - include mode*

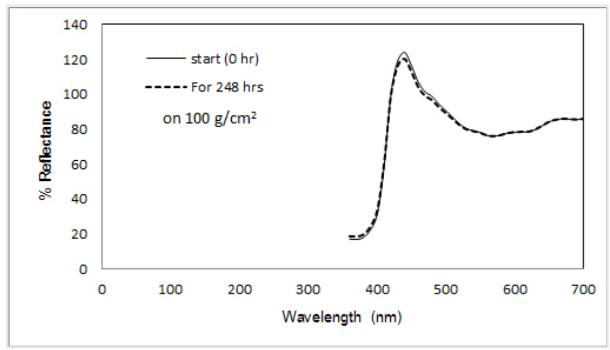

Figure 7 *Reflectance spectrum of the fluorescent inkjet ink 2 printed on plain papers of 100 g/m² before and after exposure by UVA-blacklight for 248 hrs ; measured with UV - include mode*

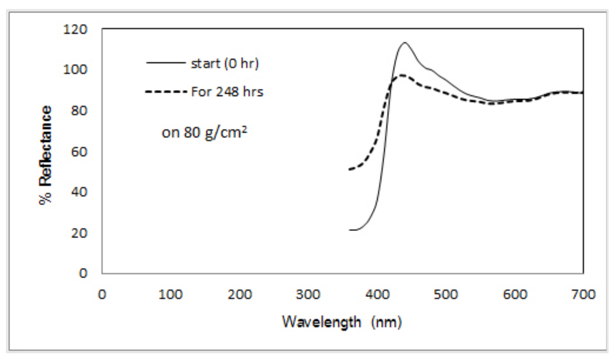

Figure 8 *Reflectance spectrum of the fluorescent inkjet ink 2 printed on plain papers of 80 g/m² before and after exposure by UVA-blacklight for 248 hrs ; measured with UV - include mode*

Visual evaluation

It was better for printing on 100 g/m² paper, the smallest text and line that could be printed with these invisible fluorescent inks with well visibility were the sizes over 6 and 0.2 pt., respectively. To avoid fading by light, it was recommended to print with the text size and line width over sizes of 14 pt. (ink 1), or 18 pt. (ink 2), and 0.2 pt. (ink 1), or 0.8 pt. (ink 2), respectively, and solid screen (see Table 4). As it was shown in Table 4 and 5, it was found that visibility on prints of ink 1under blacklight was likely better than that of ink 2, it probably was that ink1 gave better jetting than ink2 Since ink 1 was made from the UV fluorescent dye 1, which had high purity chemicals; less contamination than the dye 2, therefore the dye 1 yielded high quality of inkjet ink that it could be ejected through ink-nozzle with little clogging. Whereas ink 2 made from low purity dye 2 was not ejected through ink-nozzle as good as ink 1 did. If an inkjet ink had high clogging, it would give low ink-ejection to have low ink amount onto the printing substrate, and finally resulted in less visibility than in the case of high ink-ejection. Effect of paper type was clearly supporting the reflectance spectrum that the heavier paper of 100 g/m² had higher lightfastness, whereas the 80 g/m² paper showed poor lightfastness.

Effect of PE film lamination on the print was disturbing to visibility on the prints, that was the smallest visible size was bigger for more than double value (x2) of in case of without lamination (see Table 5 and 4, respectively). However, laminated layer of polyethylene film did not neither effect nor support on lightfastness property of the print document (see Table 5).

Table 4 Visibility under blacklight of invisible inks on prints

Inks	Paper types (g/m^2)	UVA exposure (hrs)	Smallest visible		
			Letter size (pt)	Line width (pt)	% Screen
Ink 1	100	0	6	0.2	50
		248	14	0.2	80
	80	0	14	0.2	60
		248	-	0.6	90
Ink 2	100	0	6	0.2	80
		248	18	0.4	90
	80	0	14	0.4	90
		248	-	-	-

- stands for ink disappearing or completly fading

Table 5 Visibility under blacklight of invisible inks on prints; in case of polyethylene lamination on prints

Inks	Paper types (g/m^2)	UVA exposure (hrs)	Smallest visible		
			Letter size (pt)	Line width (pt)	% Screen
Ink 1	100	0	14	0.2	80
		248	21	0.4	90
	80	0	21	0.4	60
		248	-	0.6	90
Ink 2	100	0	14	0.2	30
		248	21	0.4	70
	80	0	21	0.6	90
		248	-	-	-

-stands for ink disappearing or completly fading

Conclusion

Overall character: its ink, reflectance spectrum, and lightfastness property of dye 2 resembled of dye 1, therefore chemical of dye 2 was possibly stilbene derivative as well. But it could be compatible with inkjet printing system lesser than dye 1, perhaps due to involving of chemical purity that was not suitable enough for making an inkjet ink as good as dye 1 was. The stilbene fluorescence dye commonly used as an optical brightener could be used in an aqueous based inkjet ink as an invisible ink for an anticounterfeit document.

It was found that the printing paper had influence on lightfastness of the invisible UV fluorescent inkjet ink. The heavier weight paper with having more fiber content to absorb the liquid ink inside paper bulk resulted in better lightfastness than that of the lighter weight paper. These invisible fluorescent inkjet ink should be printed on 100 g/m2 paper, or more grammage because printing the invisible ink on 80 g/m2 paper had fast disappearing of the image. If it needed to have dry laminated, or film layer covering on the print, the text and line sizes would be increased from the sizes those of without lamination. Solid screen was suggested to be designed in the document page for printing with these invisible inkjet inks.

References

[1] B. Thompson, Printing Materials: Science and Technology, Kent: Pira International, 1998.

[2] J. A. G. Drake, Chemical Technology in Printing and Imaging Systems, Cambridge: Royal Society of Chemistry, 1993.

[3] Joanna Izdebska and Sabu Thomas, Printing on Polymers: Fundamentals and Applications, William Andrew, Elsevier, VA (2016), pp. 231-246

[4] J. Lee, S. G. Kong, T. Y. Kang, B. Kim, and OY Jeon, “Invisible ink mark detection in the visible spectrum using absorption difference”, Forensic Science International, vol. 236, pp. 77-83, 2014.

[5] S. J. Park, J. Y. Park, and H. K. Yang, “Luminescence of a novel cyan emitting Sr10(PO4)6O:Ce3+ phosphor for visualization of latent fingerprints and anti-counterfeiting applications”, Sensors and Actuators B: Chemical, vol. 262, pp. 542-554, 2018.

[6] G.R.Revannasiddappa, M.S.Rudresha, and H. Nagabhushana, “Combustion Synthesis of MgSiO3: Eu3+ (1-11 mol %) Nanophosphor: Detection of Eccrine Latent Fingerprints and Anti-Counterfeiting Applications”, Materials Today: Proceedings: Part 3, vol.5, no. 10, pp. 22473-22480, 2018.

[7] S.K.Gupta, S.L.Mukhi, and H.L.Bami, “Differentiation of inks on documents by dequenching of ultraviolet fluorescence: A case report”, Forensic Science International, vol. 12, no. 1, pp. 61-64, 1978.

[8] K.N.Venkatachalaiahab, H. Nagabhushana, G.P. Darshand, R.B.Basavaraj, and B.D. Prasade, “Novel and highly efficient red luminescent sensor based SiO2@Y2O3:Eu3+, M+ (M+ = Li, Na, K) composite core–shell fluorescent markers for latent fingerprint recognition, security ink and solid state lightning applications”, Sensors and Actuators B: Chemical, vol. 251, pp. 310-325, 2017.

[9] W. C. Xu, Y. Yang, and J. Y. Sun, “Study on Preparation and Properties of Fluorescent Offset Printing Ink", Advanced Materials Research, Vol. 174, pp. 393-396, 2011.

[10] J. Komasatitaya, “Invisible Inks using a Fluorescent pigment for Ink Jet Application”, Proceeding of Pan-Pacific Imaging Conference’08, Tokyo, Japan, pp. 402-404, 2008.

[11] G. Likhtenshtein, Applications in Chemistry, Life Sciences and Materials Science, Weinheim: WILEY-VCH Verlag GmbH & Co. KGaA, 2010.

[12] Y. Gawale, and N. Sekar, “Fluorescent pyridopyrimidine fused pyranones - design, synthesis, fluorescent whitening and DFT studies”, Jour. of Luminescence, vol. 194, pp. 248-256, 2018.

[13] G. Zhang, H. Zheng, M. G. Lun, D. Guojun, and L. P. Wang, “Synthesis of polymeric fluorescent brightener based on coumarin and its performances on paper as light stabilizer, fluorescent brightener and

surface sizing agent", Applied Surface Science, vol. 367, pp. 167-173, 2016.

[14] G. Xia, and H. Wang, "Squaraine dyes: The hierarchical synthesis and its application in optical detection", Jour. of Photochemistry and Photobiology C: Photochemistry Reviews, vol. 31, pp. 84-113, 2017.

[15] J. Y. Park, Y. Hirata, and K. Hamada, "Relationship between the dye/additive interaction and inkjet ink droplet formation", Dyes and Pigments, vol. 95, no. 3, pp. 502-511, 2012.

[16] H. Wijshoff, "The dynamics of the piezo inkjet printhead operation", Physics Reports, vol. 491, no. 4–5, pp. 77-177, 2010.

[17] H. Wijshoff, "Drop dynamics in the inkjet printing process", Current Opinion in Colloid & Interface Science, vol. 36, pp. 20-27, 2018.

[18] S. Magdassi, The Chemistry of Inkjet Inks, Singapore: World Scientific Publishing, 2010.

Author Biography

Juntira Komasatitaya, she is working as a position of Assistance Professor in King Mongkut's University of Technology, Thonburi at Department of Printing and Packaging Technology. She received Doctoral Degree in Material Engineering, Applied chemistry, Surface Chemistry Laboratory from Gifu University, Japan. Her research field is mainly in printing technology including printing ink and materials.