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Evaluating the Effect of Reactive Dye Structure and Penetrant Type on the Fastness of Ink-Jet Prints

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ABSTRACT

The purpose of this study was to investigate the effect of reactive dye structure and the type of penetrant in ink formulation on different kinds of paper ink-jet printing. Six different types of paper with different textures or gloss and the same grammage were printed upon with three commercial reactive dyes, i.e. C.I. Reactive Blue 49 (Ink 1, 4), C.I. Reactive Blue 21 (Ink 2, Ink 5) and C.I. Reactive Blue 19 (Ink 3, Ink 6), which are based on different reactive groups, chromophores and possess different numbers of anionic groups. Ethylene glycol mono butyl ether (Ink1 to Ink 3) and Ethylene glycol di-butyl ether (Ink 4 to Ink6) were used in ink formulation as penetrants. Optical density, colorimetric properties, wash and light fastness of the printed papers were evaluated. The results indicated that the printed subjects with Ink 1 to Ink 3 had less optical density, high dye penetration and good wash fastness properties compared to Ink 4 to Ink 6. Ink 2 and Ink 5 showed excellent wash and light fastness on the most of the substrates compared to other inks. A higher optical density of printed images is obtained by using glossy substrates. Prog. Color Colorants Coat. 7(2014), 73-83 © Institute for Color Science and Technology.

1. Introduction

The ink-jet printing technology has been developed for many years and in the last two decades drop-on demand (DOD) ink-jet printing system has grown to a major topic in scientific researchs [1-6]. DOD ink-jet printers are widely used in small businesses and home offices due to their low price, low noise, easiness of full coloration, low space demand, and being able to print various substrates including plain paper, paper for special printing. The two most popular types of DOD ink-jet printers are thermal [1-3] and piezoelectric [4-5]. In the thermal ink-jet printer, which is used in this research, the ink droplets are sputtered by the pressure brought about by the selective evaporation of ink that results from heating a thermocouple integrated in the ink channel of the nozzle. Three basic elements are important for ink-jet printing quality: the printing head which is used in the printer; the

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ink formulation and the printing media where the ink droplets are deposited to form an image.

Water-based inks, which have been developed increasingly for use in DOD ink-jet printing method comprise of water, water-soluble organic solvent, co-solvents and humectant to control the evaporation, and a number of materials as penetrant and coloring agent. As a coloring agent for the water-based ink used for ink-jet printing, water- soluble dyes, such as basic, acid, direct, and reactive dyes are generally used instead of pigments [7]. Optically, dyes scatter light and therefore, provide high saturated color. However, the relatively large pigment size results in increased surface roughness of the ink layer and causes light to scatter, thereby producing less saturated and duller prints. In the printing substrate, adequate ink absorbency, drying speed, light and water fastness are very important to make high superiority color images.

Good water fastness requires a critical balance of properties. For example, ink-jet printers require water soluble dye systems to avoid jet nozzle clogging, which may be obtained through improved-solubility dyes. Several researches have been done to improve the quality of ink-jet printing by producing improved water fast dye sets, [8-12] or trying new materials.

In the latter, the new materials such as cationic polymers [13-18] mixed metal cations in the form of their sulphate [19], cationic metal-organic charge complex [20], or nanoparticle metal oxide in the paper coating formulations [18] or adding nitrile to the inks formulation [21,22] used to improve the quality of ink-jet printing. The water solubility of dyes is a source of poor image water fastness. One strategy to increase water fastness is to chemically attach dyes to the substrate surface during printing by coating the paper with silica pigments [23], poly vinyl aclcohol binder (PVA), kaolin and cationic polymer additives, which are typically expensive [18,24-29]. However, water and light fastness largely remain a concern for papers. Research on improving fastness properties of ink-jet print has significantly focused on the paper coating formulations. In contrast, considerably less attention has centred on the ink formulation. Therefore, the present study has focused on the effect of reactive dye structure and the type of penetrant in ink formulation on the image quality and fastness of the ink-jet prints on different substrates. As The ink-substrate interactions are the most important mechanisms governing optical density values and penetration of ink into the substrate, six types of paper with different textures or gloss and the same grammage were used in this study. The type of penetrant and the structure of the reactive dye also play a major part in dye penetration in the substrate. This investigation was carried out using three reactive dyes with distinctive structure, which were based on different reactive groups, chromophores and the number of sulphonic acid groups. Two types of penetrants are added to the ink to evaluate the penetration of the ink into the paper.

2. Experimental

2.1. Materials

Three reactive dyes, which are based on mono-chlorotriaze or vinyl sulfone reactive group but differ in chromophore structure and the numbers of sulphonic acid groups (Table 1) were kindly provided by Alvan Sabet Company, Iran.

Polyethylene glycols 200, isopropyl alcohol, 2-pyrrolidone as co-solvents were received from Merck Company, Germany. Ethylene glycol mono-buthyl ether and Ethylene glycol di-butyl ether as penetrant were also provided by Merck Company, Germany (Table 2). Six types of papers (Table 3) with different textures, glosses or whiteness, and the same grammage were used in this study.

2.2. Equipments and instrumentation

The prepared inks (Ink1 to Ink6) were filtered through 0.45 and 0.2 µm Sartorius Minisart filter (Göttingen, Germany). The different coated papers were ink-jet printed using a HP DeskJet 5150 printer. The reflectance measurements of the prints were determined using a Gretag Macbeth Spectrophotometer ColorEye7000A (New York, USA) with d/8ºmeasurement geometry under the following conditions: measurement wavelength range from 400nm to 700nm, measurement area of 10mm in diameter, and the specular component included (SCI) measurement mode.

The CIELAB values were computed under D65 illuminant and CIE 1964 (10°) standard observer. The pH, surface tension and viscosity of inks were characterized using 827 pH Metrohm meters (Herisau/ Switzerland), Tensiometer K100MK2 (Hamburg, Germany) and Brookfield DVII (New Jersey, USA), respectively.

Table 1: Dyes used in ink formulation.

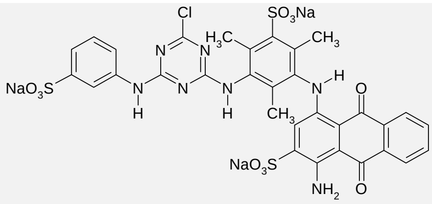
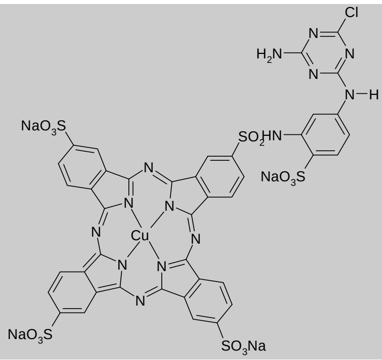
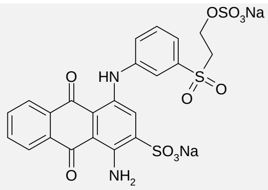
Ink	Dye	Structure of dye
1,4	C.I. Reactive Blue 49	
2,5	C.I. Reactive Blue 21	
3,6	C.I. Reactive Blue 19	

Table 2: Penetrants used in ink formulation.

Ink	Penetrant
1,2,3	Ethylene glycol mono butyl ether
4,5,6	Ethylene glycol di butyl ether

Table 3: The substrates used for printing.

Substrate	Weight (g/m^2)	Finish	Paper	Compatibility
1	260	high glassy	photo Ink-jet Paper	Epson, HP, lexmark and canon ink-jet printer
2	260	wave	premium Photo Paper	all ink-jet printer
3	260	pearl	photo paper Premium Plus	all ink-jet printer
4	260	glossy	photo paper Premium Plus	all ink-jet printer
5	260	satin	quality photo satin paper plus	all ink-jet printer
6	260	glossy	quality photo glossy paper plus	all ink-jet printer

The cross sectional view of the printed paper was verified using a Dino Lite AM413-T8 Handheld Digital Microscope to determine the penetration of the ink into the paper. The optical densities of the printed subjects were measured using spectrodensitometer Ihara S900. The color fastness of the ink-jet printed papers to light and washing were determined by ASTM F2366-05 and ASTM F 2292 – 03, respectively.

2.3. Printing of ink on substrate

The ink-jet printing was carried out with HP DeskJet 5150 printer at 1200dpi using the ink formulation as shown in Table 4 onto different types of paper. The pH of the ink was adjusted to 7-7.5 by McIlvaine buffer solution composed of disodium hydrogen phosphate ($82.35 cm^3$, 0.2mol) and citric acid ($71.65 cm^3$, 0.1mol) to prevent print-head and cartridge from damaging. Then solid single color area was printed on different white papers to compare the fastness and print quality of printed paper. The physical properties of the prepared ink are shown in Table 5.

2.4. Optical density

Generating vibrant images on paper is one of the primary goals of printing. A parameter used to quantify the darkness of prints is the optical density, $OD = -\log(I/I_o)$, where I_o is the intensity of the incident light on a print, and I is the intensity of the light reflected from a print. Alternatively, color coordinates such as L^* a^* b^* are also used to quantify color prints, where L^* is the luminance, a^* represents the red/green balance of a color, and b^* the yellow/blue balance.

2.5. Wash fastness test

The water fastness properties of the prints were assessed by using the ASTM /F2292-03 water fastness test [28]. One of the two prepared printed ink-jet test samples was submerged in a pan full of distilled water at room temperature.

After 10 min, the sample was pulled out of the water, and it was dried after draining off the excess water. The color change of the patches before and after washing was computed by CIELAB 1976 color difference formula was shown as a measure of water fastness.

Table 4: The ink composition.

Ink composition	
Dye	3%
Polyethylene glycol 200	15%
2-pyrrolidone	7%
Penetrant	10%
Isopropyl alcohol	4%
De-ionised water and buffer solution	61%

Table 5: Physical properties of prepared inks.

Ink	pH	Surface tension (mN/m)	Viscosity (mpas)
1	7	29.07	2.8
2	7	29.52	2.3
3	7	28.75	2.5
4	7	30.44	3.1
5	7	29.83	3.5
6	7	28.98	2.5

2.6. Light fastness test

The light-fastness of the printed ink-jet media for specified periods of time is pertinent to the end use of these materials. The image stability is very dependent upon the wavelength distribution of the exposing illumination. The end use of printed subjects is indoor home lighting condition. Therefore, this practice is intended to produce the color changes that may occur in ink-jet prints upon exposure to irradiation from xenon arc lamp. The accelerated procedure implemented in this practice is intended to provide a means for the rapid evaluation of light fastness under laboratory conditions. The color change of the patches before and after exposing to light computed by CIELAB 1976 color difference formula, was shown as a measure of light fastness.

3. Results and discussion

3.1. The colorimetric properties of ink-jet prints

To investigate the influence of the structure of reactive dyes on the printing of paper, three blue reactive dyes, which are based on mono-chlorotriazinyl or vinyl sulfone reactive group but differ in chromophore structure and numbers of sulphonic acid groups (Table 1) were employed; C.I. Reactive blue 49(Ink 1), and C.I. Reactive blue 21 (Ink 2) and C.I. Reactive blue 19(Ink 3). Table 6 and Figures 1-2 show the colorimetric properties of Ink 1 to Ink 6.

The printed subject with Ink 2 and Ink 5 in which the reactive dye structure contains copper phthalocyanine as chromophore, have lighter shade (higher L* value) than the others. Also, a* and b* values of Ink2 and Ink5, which are different compared to a* and b* values of other inks (Ink1, Ink3, Ink4 and Ink6) prove that the color of the Ink2 and Ink 5 are cyan. However, the printed subjects with Ink1, Ink3, Ink4 and Ink6 which have blue color are similar in L*a* and b* value, since they have equal chromophore (anthraquinone) in their reactive dye structure. This shows that the shade of the inks appeared to be dependent on the type of chromophore in reactive dye structure. The printed subjects with Ink1 to Ink 3 have lighter shade (higher L* value) than the printed subjects with Ink4 to Ink6. This proves that ethylene glycol mono butyl ether have more influence on penetrant ink than ethylene glycol di-butyl ether due to its lower molecular weight.

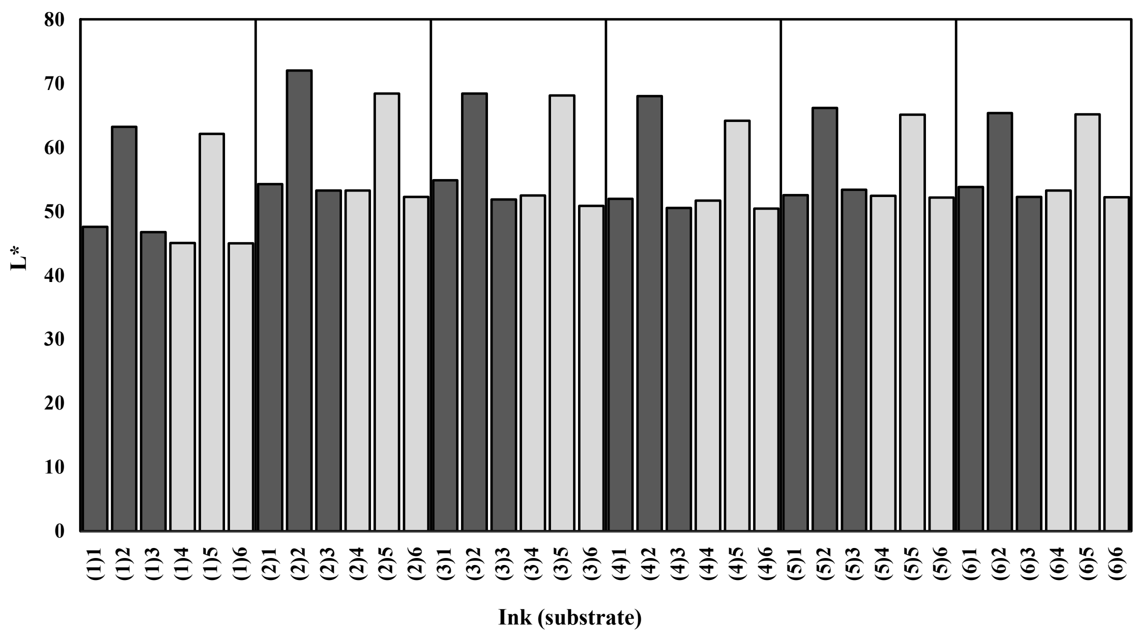


Figure 1: The L^* value of printed subject with Ink1 to Ink 6 on different substrates (substrate 1 to substrate 6).

Table 6: The colorimetric data, percentage of penetration, wash and light fastness of printed subject with Ink1 to Ink 6 on different substrate.

Substrate	Ink	L*	a*	b*	OD	Penetration(μm)	Wash fastness(ΔE)	Light fastness(ΔE)
1	1	47.6	3.19	-48.08	0.95	36.63	1.45	4.20
	2	63.2	-37.8	-36.57	1.4	42.43	1.01	3.95
	3	46.7	2.23	-50.73	1.11	29.3	1.31	5.96
	4	45	3.14	-47.39	1.04	30.5	2.5	-
	5	62.1	-40.5	-35.66	1.45	39.14	1.27	-
	6	45	2.44	-49.98	1.19	20.57	3.32	-
2	1	54.2	-1.26	-43.15	0.78	42	1.98	10.84
	2	72	-34.18	-28.80	0.99	58	1.3	1.35
	3	53.21	-3.92	-47.22	0.94	38	1.86	9.30
	4	53.24	-0.44	-43.61	0.81	31	2.66	-
	5	68.4	-39.12	-30.06	1.08	33	2.36	-
	6	52.2	-2.61	-47.97	0.98	26	3.6	-
3	1	54.82	0.41	-47.49	0.77	43.6	3.45	8.27
	2	68.37	-37.40	-33.01	1.13	57.6	1.35	1.65
	3	52	-2.79	-49.40	0.99	35.1	5.46	6.20
	4	52.48	-1.42	-43.47	0.96	36	3.98	-
	5	68.1	-38.37	-31.95	1.18	38	1.45	-
	6	50.8	-3.41	-48.61	1.02	25	6.97	-
4	1	51.94	-1.25	-45.41	0.86	41.33	1.56	7.15
	2	68	-41.08	-31.74	1.29	54.2	8.93	1.90
	3	50.51	-4.63	-49.25	1.1	34	1.55	6.70
	4	51.64	-1.34	-44.33	0.9	31.5	5.62	-
	5	64.11	-44.28	-34.25	1.69	35	5.6	-
	6	50.43	-3.08	-49.46	1.06	17	4.3	-
5	1	52.49	-3.39	-43.64	0.8	42	6.08	8.10
	2	66.12	-41.67	-31.96	1.36	53	1.58	0.94
	3	53.36	-6.14	-46.65	0.99	35	6.59	7.21
	4	52.41	-2.79	-42.39	0.88	31	8.1	-
	5	65.09	-43.49	-32.02	1.42	36	1.59	-
	6	52.14	-5.37	-46.84	1.02	17	7.97	-
6	1	53.8	-3.19	-45.79	0.72	43	3.75	3.70
	2	65.33	-44.97	-34.95	1.68	55.3	0.9	1.42
	3	52.2	-7.48	-46.28	0.98	33	3.2	4.2
	4	53.22	-3.55	-42.63	0.79	32	6.45	-
	5	65.13	-46.64	-35.11	1.7	43	1.66	-
	6	52.17	-7.35	-45.95	1	14	5.34	-

The optical density values of the printed subject with Ink1, Ink3, Ink4 and Ink6 are similar in most types of the substrates. However, the optical density values of printed subject with Ink 2 and Ink 5 are higher than the others. The optical density values of printed subject with Ink 3 and Ink 6 are higher than the optical density values of printed subject with Ink 1 and Ink4. Ink1, Ink 3, Ink 4 and Ink 6 all are based on anthraquinone chromophore but differ in the number of sulphonic acid groups and the type of reactive group. The Ink 1 and Ink 4 both are possess three sulphonic acid groups. The Ink3 and Ink6 both are possess one sulphonic acid group. In this case, the solubility of the ink through the paper increases by the number of sulphonic acid groups. Therefore, due to the increase in ink penetration, the lighter shade and lower optical density of the printed fabric (lower L* value) were achieved.

3.2. The ink-substrate interaction

The ink-substrate interactions are arguably the most important mechanisms governing optical density values and penetration of ink into the substrate. These are highly dependent on drop spreading, which is governed by the viscosity and the surface tension of the ink as well as the absorption properties of the substrate. A range of papers can be used with ink-jet inks, and good printability depends on a number of factors. Results in Figure 2 show a higher optical density for printed images produced by using glossy substrate (Substrates 1, 4, 6). On glossy media (Substrates 1,4, 6), such as photo paper, surface reflection can be focused away from the eye. Thus, glossy prints typically have higher optical density than those on other papers (Substrate 2).

On wave paper (Substrate 2), keeping colorants on or near the surface can be challenging due to have pores on paper which able to absorb more ink into the paper.

For this reason, printed subject on the substrate 2 offers lighter shade due to its higher inks penetration in comparison with the other substrates. Pearl paper (Substrate 3) contains very special pearly mica crystals, which is based on the natural mica; they are covered with a thin layer of metal oxides. The pearl-like crystals are visible because of scattering and interference of light waves on the crystals. Porous papers have small pores in their coating, which rapidly draws water further into the paper, resulting in a print dry to the touch.

Satin paper (Substrate 5) has some sheen to it and is considered more reflective than wave paper but less than that of glossy paper.

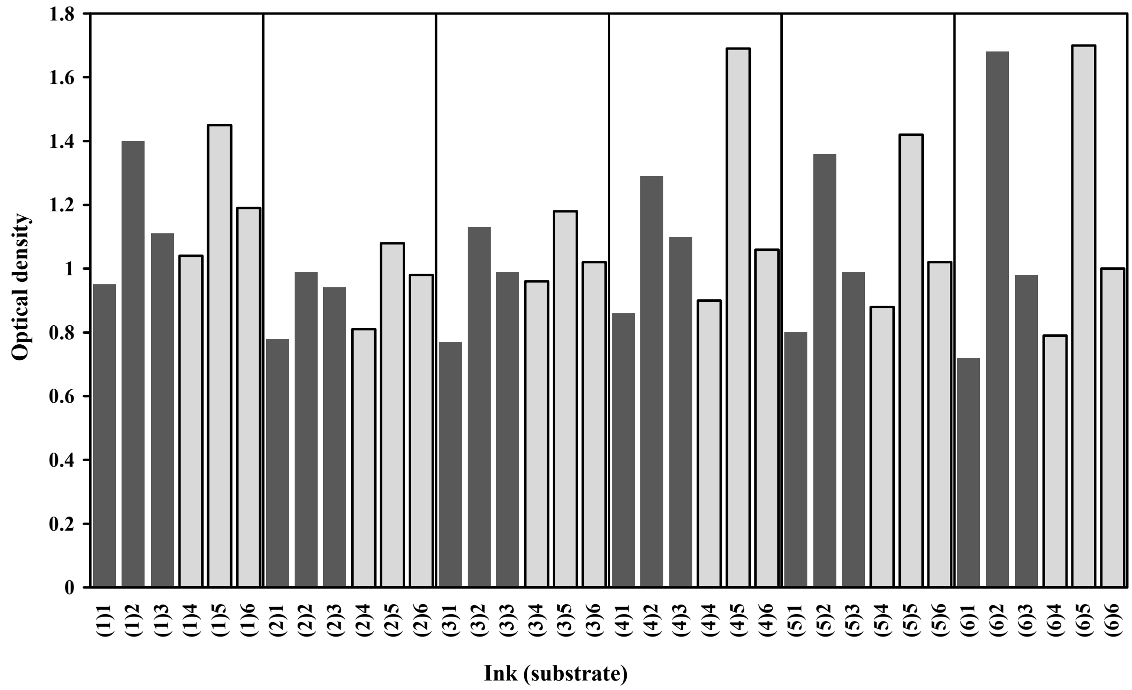


Figure 2: The optical density value of printed subject with Ink1 to Ink 6 on different substrates (substrate 1 to substrate 6).

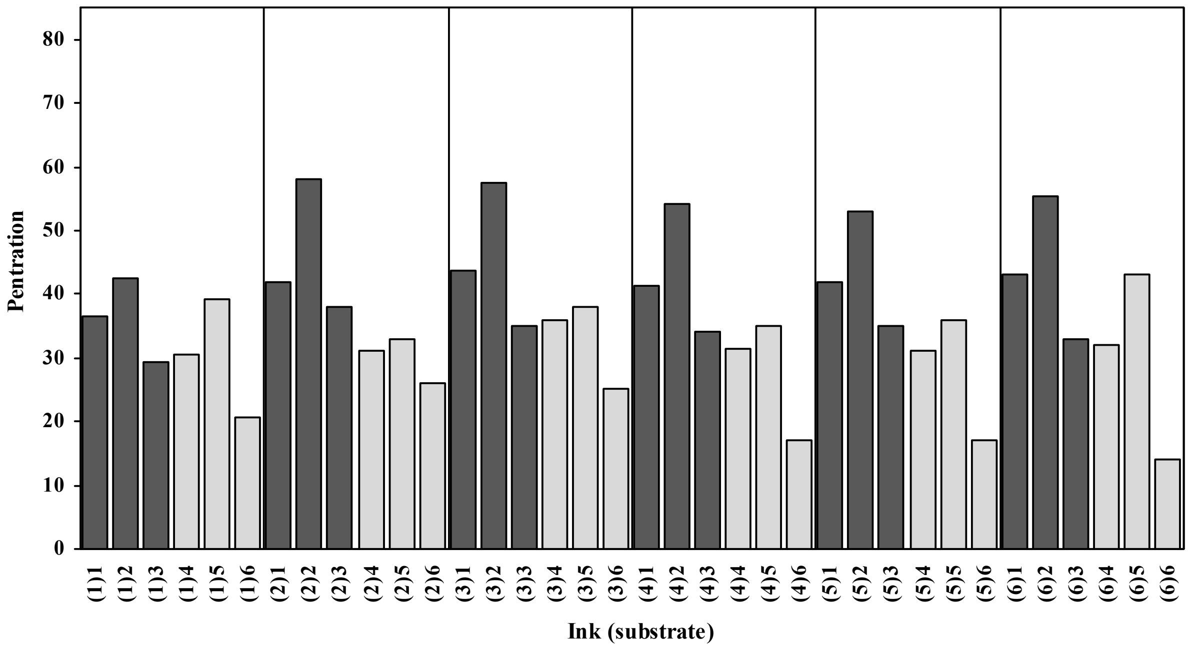


Figure 3: The penetration of Ink 1 to Ink 6 into different substrates (substrate 1 to substrate 6).

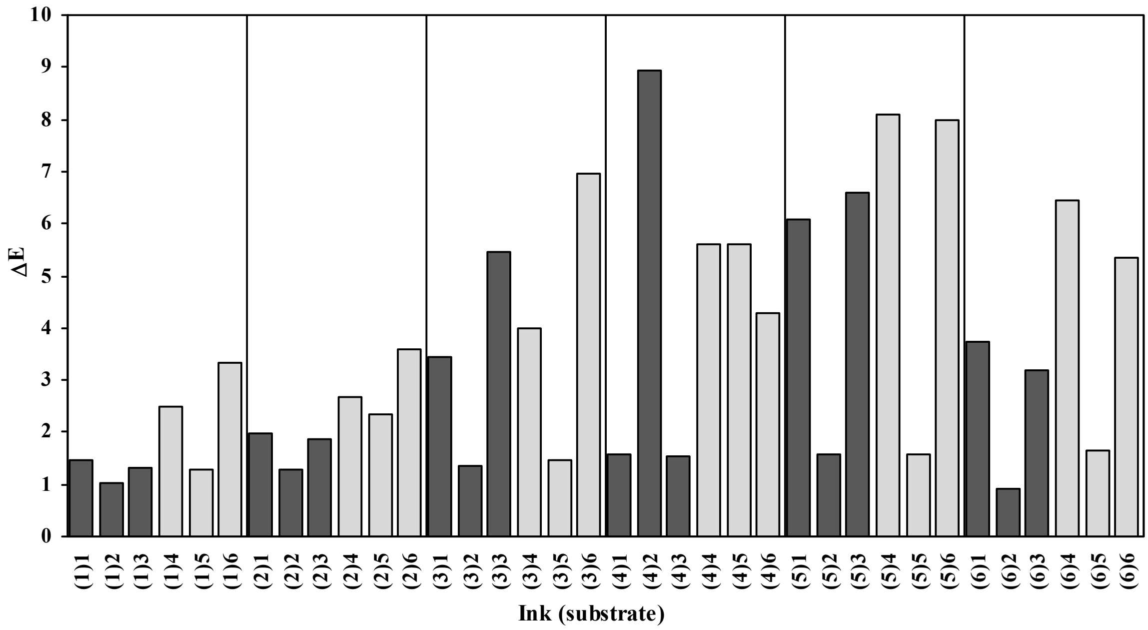


Figure 4: The wash fastness results for printed subject with Ink1 to Ink 6 on different substrates (substrate 1 to substrate 6).

3.3. Effect of ink formulation on wash fastness

The change in the shade of the patches before and after exposing to water was assessed by the CIELAB 1976 color difference formula to measure wash fastness. From the results in Table 6 and Figure 4 it can be seen that analogous to optical density of the printed subject and penetration of the ink into the substrate, the wash fastness also appeared to be dependent on the dye structure and the type of penetrant in ink formulation and substrate sort.

Very good wash fastness of printed subject is observed for Ink 2 and Ink 5 on most types of substrate except substrate 4. It can be seen that the wash fastness results for the printed subject with Ink 1, Ink 3, Ink 4 and Ink 6 are dependent on the substrate type. In substrates 1 to 3, the wash fastness result for the printed subject with Ink 1 is better than Ink 3, and the Ink 4 is better than Ink 6 as well.

Ink1, Ink 3, Ink 4 and Ink 6 all are based on anthraquinone chromophore but differ in the number of sulphonic acid groups and the type of reactive group. The wash fastness result for the printed subjects with Ink1 to Ink 3 is better (lower ΔE value) than that of Ink4 to Ink6. This proves that ethylene glycol mono butyl ether had more influence on penetrant ink into paper than ethylene glycol di-butyl ether. Therefore, the wash fastness results were improved by increasing the penetration.

Ink 1 and Ink 4 have more sulphonic acid groups compare to Ink 3 and 6. In this case, as the number of sulphonic acid groups increased the solubility of the ink through the paper increase. Therefore, due to the increase in penetration of ink through the paper, wash fastness results of the printed fabric enhances (lower ΔE value) in some of the substrates (substrates 1, 2 and 3) except substrate 6. In other substrate, the wash fastness results for printed subject with Ink 3, 6 and 1, 4 are similar and need further investigation.

3.4. Effect of ink formulation on light fastness

The color change of the patches before and after exposing to light was assessed by the CIELAB 1976 color difference formula to measure the light fastness. It is evident from the results in Table 6 and Figure 5 that the color change of the printed samples with Ink 2, in which the reactive dye structure contains copper phthalocyanine as chromophore, was much lower than the color change of the printed samples with other inks which have equal chromophore (anthraquinone) in their reactive dye structure.

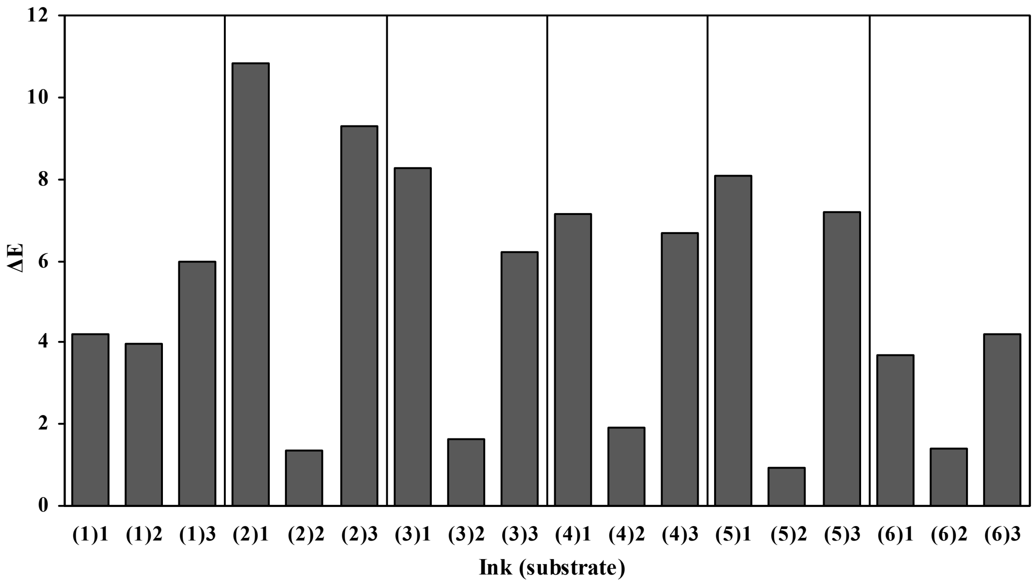


Figure 5: The light fastness results of printed subject with Ink1 to Ink 6 on different substrate (Substrate 1 to Substrate6).

Additionally, the most penetration into the paper was observed for Ink 2. Moreover, In Ink 3, Ink1 and Ink2, the number of sulphonic acid group increased respectively This shows that the light fastness of the printed subjects appeared to be dependent on the penetration of ink into the paper, which in turn depends on the sulphonic acid group numbers.

On the other hand, regarding the fading of the dye by light, there are known various decomposition paths, it is anticipated that evading the fading path to occur in an oxidative atmosphere is important.

Ink 2 and Ink 5 contain copper phthalocyanine as chromophore in their dye structure; copper phthalocyanine dye has an extremely high light-fastness, excellent color hue and coloring power. Furthermore, when a strong electron withdrawing group is introduced into the ß-position to increase the oxidation potential, then the ozone-fastness of the resulting dye can be greatly enhanced.

3.5. Effect of ink formulation on ink penetration into the substrates

Despite adding penetrants to the ink formulation to promote penetration of the ink into the paper, the structure of dye molecules in ink's formulation and the type of the substrates play an important role in penetration of the ink into the paper. According to the results in Table 6 and Figure 3, the penetration of the Ink2 and Ink5 into the printed paper is higher than the other Inks. Ink2 and Ink 5 are based on same reactive group. However they have different number of sulphonic acid groups and chromophore compare to other inks. The penetration of Ink3 and Ink6 into the printed papers is lower than the penetration of Ink1 and Ink4, which confirms the previous results for printed subjects with Ink 3 to Ink 6 that have darker shade, and higher optical density values (Figure 2) than the printed subjects with Ink1 and Ink 4.

In this case, by increasing the number of sulphonic acid groups the solubility of ink into the paper increased. Therefore the number of sulphonic acid group plays an important role on the ink penetration into paper. The penetration of Ink 1, Ink 2 and Ink 3 is higher than the penetration of Ink 4, Ink5 and Ink 6, which proves the previous results for printed subjects with Ink 1 to Ink 3 that have lighter shade and lower optical density values than the printed subjects with Ink 4 to Ink 6. This confirms that the ethylene glycol mono butyl ether have more influence on penetrated ink into the paper than ethylene glycol di-butyl ether. Therefore, the structure of reactive dyes, substrate type and the type of penetrant in ink's formulation all play an important role in the penetration of ink into the paper.

4. Conclusion

The effect of reactive dye structure and the type of penetrant in ink formulation on different kinds of ink-jet printing papers was investigated. Six types of papers, which have same grammage was printed with six inks, that contain three commercial reactive dyes, C.I. Reactive Blue 49 (Ink 1, Ink 4), C.I. Reactive Blue 21 (Ink 2, Ink 5) and C.I. Reactive Blue 19 (Ink 3, Ink 6). Ethylene glycol mono butyl ether (Ink 1 to Ink 3) and Ethylene glycol di-butyl ether (Ink 4 to Ink 6) were used in ink formulation as penetrant.

The printed subject with Ink 2 and Ink 5 in which the reactive dye structure contains copper phthalocyanine as chromophore, have lighter shade (higher L* value), higher optical density values, higher penetration into the substrate and their printed image have very good wash, and light fastness properties compared to other inks.

The printed subjects with Ink 1, Ink 3, Ink 4 and Ink 6 are similar in L*a* and b* values, since they have equal chromophore (anthraquinone) in their reactive dye structure. Therefore, the shade of the inks appeared to be dependent on the type of chromophore in reactive dye structure. The printed subjects with Ink 1 to Ink 3 have lighter shade (higher L* value), lower optical density values, higher penetration into the substrate and better wash fastness properties than the printed subjects with Ink 4 to Ink 6. This proves that ethylene glycol mono butyl ether had more influence on ink penetration into paper than ethylene glycol di-butyl ether.

The light fastness of the printed subjects appeared to be dependent on the penetration of ink into the paper and the type of chromophore in reactive dye structure. The penetration of Ink 3 and Ink 6 into the printed papers is lower than the penetration of Ink1 and Ink4, which confirms the previous results for printed subjects with Ink 3 to Ink 6 that had darker shade and higher optical density values than the printed subjects with Ink1 and Ink 4. Therefore, the structure of reactive dyes, substrate type and the type of penetrant in ink's formulation all play an important role in penetration of ink into the paper. The results regarding to the type of paper showed that a higher optical density of printed images is produced by using glossy substrates. On glossy media, surface reflection can be focused away from the eye. Thus glossy prints typically have higher optical density than those on other papers.

On porous paper, keeping colorants on or near the paper can be challenging due to have pores on paper which able to absorb more ink into the paper.

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