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Synthesis of fluorescence inks based on imino Qumarin Derivatives and Their Application in Textile Printing

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Abstract

Preparation of fluorescent three inkjet inks based on N-(4-bromophenyl)-2-(2-imino-2H-chromen-3-yl) benzo[d]thiazole-5-sulfonamide derivatives the structures of compounds are confirmed via, element analysis, IR, H-NMR, and Mass spectra , microencapsulation and surface modification methods are used to prepare the inks, then printed on polyester, polyamide and paper, by inkjet printing technique as a printed security features. The prints posse very good fastness properties and high fluorescence emission

Introduction

It is well documented that coumarin compounds and its derivatives play an important role in organic chemistry, they are an important group of fluorescent organic dyes [1-7]. They have a special significance as yellowish-green fluorescent dyes. The most important coumarin fluorescent dyes contain heterocyclic fused ring such as coumarin 6, coumarin 7. They act as fluorescent labels and pigments [8], as fluorescent probes for physiological and enzymatic measurements, as sensors and in advanced photo physical systems [9-10].

Inkjet printing is a patterning technique which offers efficient process, ease of use, low cost and environmental impact Inkjet is the only non-contact printing method thus enabling the use of a variety of substrates [11-12]. Inks formulation plays an important role in determining the printing quality [13-14]. So the this research was carried out to prepare some fluorescent coumarin dyes containing N-alkyl sulfonamide groups to use in preparation of fluorescent inkjet inks, then printed on polyester, polyamide and paper, by inkjet printing technique as a printed security features.

Materials and Methods

Chemical and Reagents:

Ethyl alcohol (99.9% pure grade), Salisaldehyde ($C_7O_2H_8$), Ethyl acetoacetate, ($C_6O_3H_{10}$). Pipridine. 4-N, N-diethyl salisaldehyde, ($C_{11}O_2NH_{15}$). 2-cyanomethylbenzimidazole, ammonium acetate, chlorosulfonic acid, 4-sulphatoethyle vinyl sulphone benzyl amine, 4-bromo benzyl amine, diethylene glycol, glycerol, urea, sodium hydroxide, poly vinyl alcohol, Turkey and acrylate binder. Bi-distilled water and de-ionized water. All of the chemical were used as received without further purification.

- Polyester, polyamide and paper A4 (80gm^2 and 60 gm^2) as a substrate for printing.

Dynamic Viscosity (η):

Dynamic Viscosity of the prepared ten inkjet inks measured by using Brookfield Model Dv – 111, programmable R geometer, USA.

Luminescence images of the printed Samples:

The printed paper and textile fabric samples were investigated by Video Spectral Comparator (VSC 6000). The printed paper and textile fabric samples was placed in the VSC chamber and the image was displayed on the monitor in VSC software. The samples were illuminated with Ultraviolet light by pressing Ultraviolet option with band pass filter < 400 nm and long pass filter off. The image was focused by pressing the +ve or –ve sign of focus option of VSC software and by rotating the knob for fine focusing. This dotted pattern was seen on the entire surface of the sample. Then the images were

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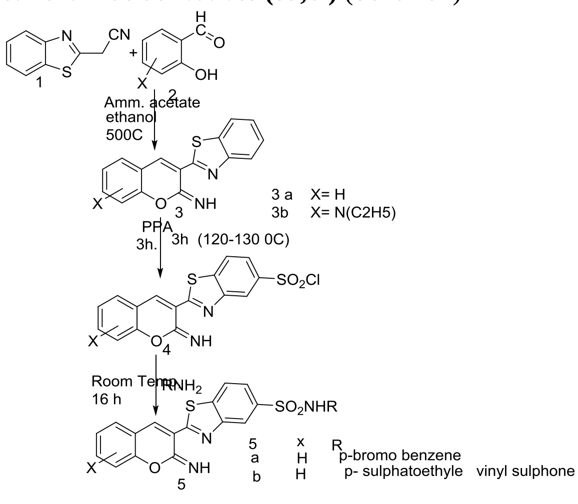
saved into the computer hard drive through VSC software.

Synthesis:

The basis of the synthesis of the coumarins **(3a and b)** 3-(benzo[d]thiazol-2-yl)-2H-chromen-2-imine derivatives **(3a and b)** (Scheme I.) is the base-catalysed condensation of 2-cyanomethylbenzimidazole 1 with 2-hydroxybenzaldehyde derivatives 2 in ethanol (30 mL) in a flask in the presence of ammonium acetate, and the reaction mixture was monitored by TLC. After the reaction was completed, the reaction mixture was cooled to room temperature. The precipitate was filtrated and recrystallized using EtOH, which forms iminolactones 3 [11].

A mixture of (E)-4-(2-(benzo[d]thiazol-2-yl)-3-iminoprop-1-en-1-yl)-N,N-diethylaniline **(3b)** (0.011 mol) and chlorosulfonic acid (0.26 mol) was stirred for 2- 3 h at 120-130 ˚C. The reaction mixture was cooled to 10 ˚C and poured into cold water (200 g). The precipitate was collected and washed with cold water until the washings were about pH5. The filter cake was transferred to a 3-necked flask along with 5 ml water (as solvent) and amine (0.02 mol) was added, keeping the temperature below 10 ˚C. The reaction mixture was kept for 2 h at room temperature, then filtered off and washed with water until the washings were colourless. The product was dried in vacuum at 60 ˚C for 8 h to give dye 2-(2-imino-2H-chromen-3-yl)benzo[d]thiazole-5-sulfonamide derivatives **(5a,b)** (Scheme I)



(Scheme I): Synthesis of iminocoumarine dyes.

Printing Experiment:

. Ink Jet Printing:

Inkjet printing experiments were carried out on paper, polyester fabric and polyamide fabric using the produced luminescent nan prepared fluorescent dyes.

Preparation of Ink Jet Inks.

Ink Jet Inks were prepared by varying the dispersed prepared nano-fluorescent dyes either by the micro-encapsulation technique or the surface modification technique.

Micro-Encapsulation Technique:

Inkjet inks is prepared by 3_b fluorescent dye with a pigment-to-polymer ratio of 2:1. The formulation in a weight basic for preparing the pigmented ink jet ink is shown as follows: pigment dispersion 8%, diethylene glycol 10%, glycerol 10%, urea 5%, polyvinyl alcohol (PVA) 4% and de-ionized distilled water, 63%. The ink components were mixed together by ultrasonic (Sonics and materials inc model vcx 750 volts 230 vac) at 100 rpm for 10 min or 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 a 8μm pore filtering sieve. After the inks had been prepared, they were stored in capped glass vessels and placed in a desiccators to avoid absorption of moisture from the air**.** then the inks were loaded into the inking unit of the modified printer (HP DeskJet 1050 A PRINT SCAN COPY).[10]

Surface Modification Technique.

Three inkjet inks were prepared by varying the dispersed of (3_b) and (5_a and $_b$) prepared fluorescent dyes with a dye to binder ratio of 1:2. The formulation in a weight basic for preparing the ink jet inks is shown as follows: dye dispersion 4%, diethylene glycol 10%, glycerol 10%, urea 5%, binder 8% and de-ionized distilled water, 63%. The ink components were mixed together by ultrasonic (Sonics and materials inc model vcx 750 volts 230 vac) at 100 rpm for 10 min or 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 a 8μm pore filtering sieve. After the inks had been prepared, they were stored in capped glass vessels and placed in a desiccators to avoid absorption of moisture from the air Then the inks were loaded into the inking unit of the modified printer (HP DeskJet**)**

Inkjet Printing on Fabric.

HP inkjet printing are ideal for printing on fabric because they spray beautiful color evenly on cloth. HP all in one printers print on fabric too, and their scan function allows us to create original design of everything.

Printing steps:

*Take sheet of paper (60 gm^2), and cover the work surface (it is beast to do it outside, because the spray gets everywhere). Once covered, place the sheet of cardstock down and lightly spray over the whole piece.

*Gently pick up the card stock, place it adhesive side down on to apre-ironed piece of fabric (polyester and polyamide), and smooth it all down with your hands so its wrinkle free. It work best to start from the center and work to the edges.

*Trim around the cardstock with fabric scissors (cut any stray threads). Now fabric is ready to print on.

*Select your image and use the fabric facing the print direction of computer, (Min is face down). After it prints, give it about 10 min or so for the ink to dry.

*Peel the paper off of the cardstock.

Figure (1): The Steps of Preparing Fabric (Polyester and Polyamide) for printing by Inkjet

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Measurements and Analysis

The melting points for synthesized dyes were investigated using a melting point apparatus. FT-IR, nuclear magnetic resonance, Mass spectra. Perkin Elmer double-beam spectrophotometer is used to measure Absorption spectra. Steady – state fluorescence measurements were performed at room temperature using Shimadzu RF5301 Spectro fluorophotometer in the range (290 – 750 nm). The prepared dyes were dissolved in absolute ethanol at a concentration of 10^{-6} mole/l. Color strength values of the printed samples were measured using reflection spectroscopy (Hunter Lab Ultra Scan PRO USA, 2007) at the wavelength of the maximum absorbance and it was expressed as K/S which assessed by applying the Kubelka–Munk equation [4-8].

Fastness properties of printed fabrics to washing, crocking (dry and wet rubbing), perspiration and light were determined according to standard methods AATCC Test Method 61-2007, AATCC Test Method 8-2007, AATCC Test Method 15-2013, AATCC Test Method (16-2004) respectively. The evaluation established using the blue scale as reference of colour change [15-18].

Results and Discussion

The Established and Confirmed the Structures of the Synthesized Fluorescent Coumarin Dyes: Elemental analysis and spectral data (IR, ^{1}HNMR and Mass Spectra) of the synthesized Dyes.

According to the dye structure, all the synthesized compounds (3_b - $5_{a\ and\ b}$) are confirmed on the basis of their physical data and spectral analysis shown in Tables (1.2, 3, 4 and 5),

Table 1: Physical and Chemical Data of Synthesized Dyes (3_b and $5_{a\ and\ b}$).

Dye	Color	Yield %	M.P ˚C	Molecular Formula	M. Wt.
3b	orange	98	160	$C_{20}H_{18}ON_3S$	306
5a	Brownish Yellow	90	180	$C_{22}H_{14}O_3 N_3 S_2 Br$	512
5b	yellow	88	175	$C_{24}H_{19}O_9 N_3 S_4 Na$	643

Table 2: FTIR Data of Synthesized Dyes (3_a and $5_{a\ and\ b}$).

Dye No.	NH	CH alkyl	C═O	Ar C─ C	SO_2NH
3b	**3050**	**2923**	**1714**	**1594**	**1510, 1460, 1349 1267, 1196, 1124**
5a	**3096**	**2917**	**1718**	**1568**	**1510, 1483, 1393 1158, 1078, 1024**
5b	**3074**	**2979**	**1719**	**1527**	**1560,1482, 1325 1144, 1041, 1020**

Table 3: ^{1}H-NMR of synthesized dyes ($5_{a\ and\ b}$).

Dye	^{1}H-NMR
5a	3.4(t, 2H, CH_2), 3.66(t, 2H,CH_2), 6.92(d, 2H, CH), 7.09- 8.73(m, 9H,C_6H_4), 9.30(s, H, NH) beak for =NH did not appear due to resonance
5b	3.4(t, 2H, CH_2), 3.66(t, 2H,CH_2), 7.2-8.39(m, 11H,C_6H_4), 9.26(s, H,NH) beak for =NH did not appear due to resonance

Table 4: Elemental Analysis and Mass Spectra of Synthesized Dyes (3_a and $5_{a\ and\ b}$).

Dye No.	Elemental analysis						Mass Spectra(M^{+1})
	Calculated (%)			Found (%)			
	C	H	N	C	H	N	
3a	62.2	4.87	8.06	62.41	4.85	8.09	307
5a	62.07	4.57	8.11	62.05	4.59	8.13	510
5b	62.02	4.75	8.15	62	4.82	8.16	644

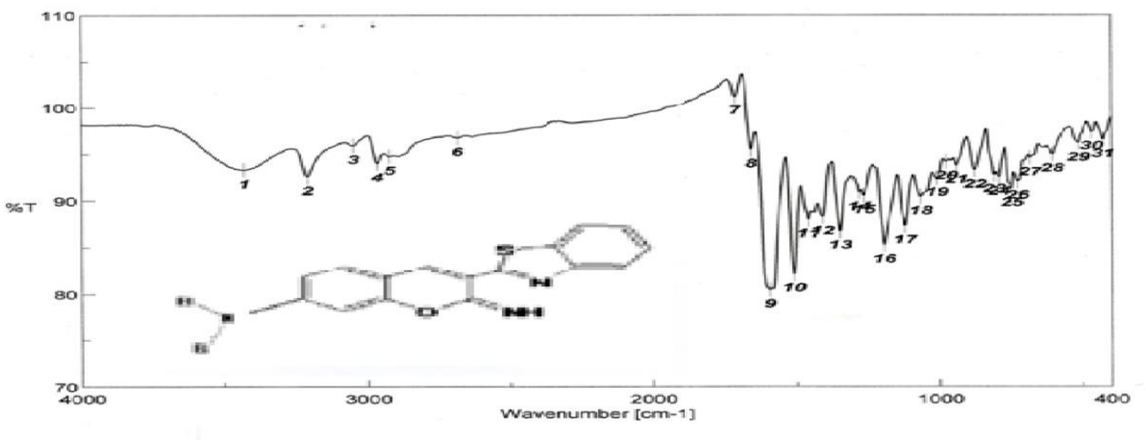


Figure (2): FTIR Spectra of Synthesized 3b Dye.

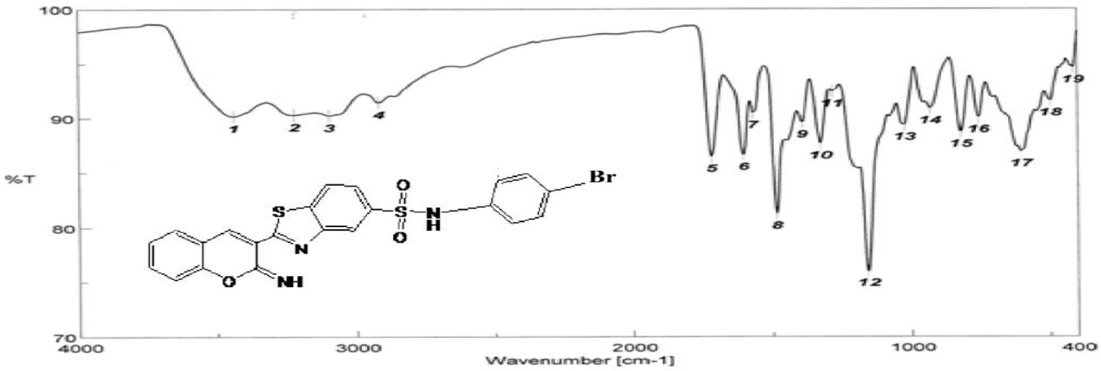


Figure (3): FTIR Spectra of Synthesized 5a Dye.

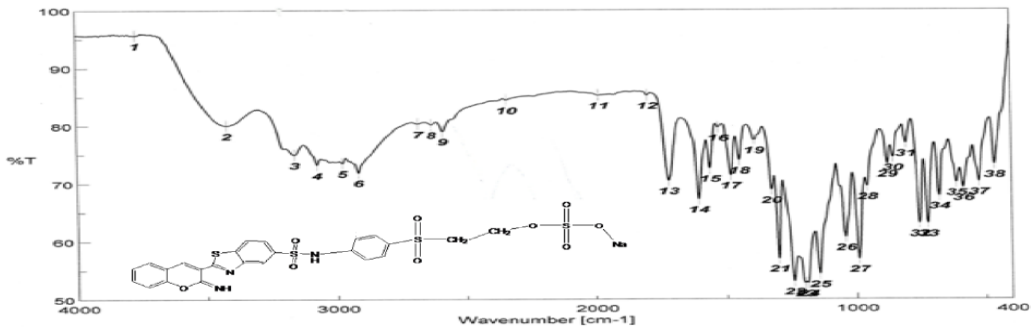


Figure (4): FTIR Spectra of Synthesized 5b Dye.

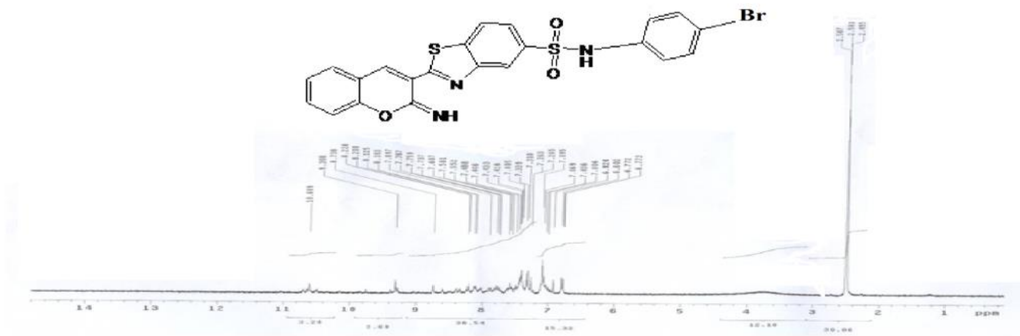


Figure (5): ¹H-NMR of Synthesized 5a Dye.

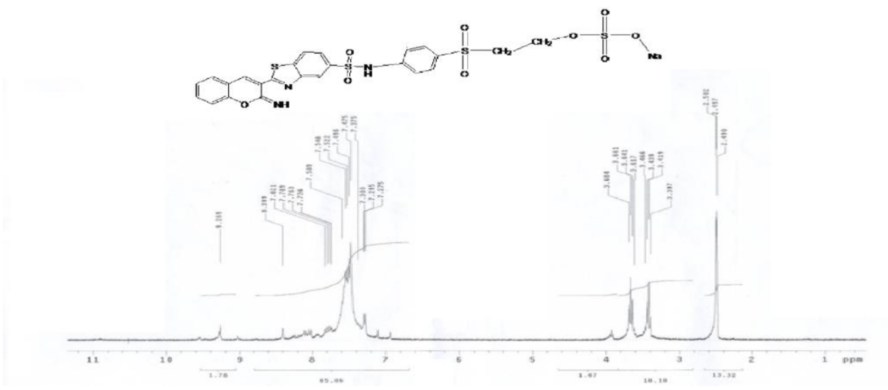


Figure (6): ¹H-NMR of Synthesized 5b Dye.

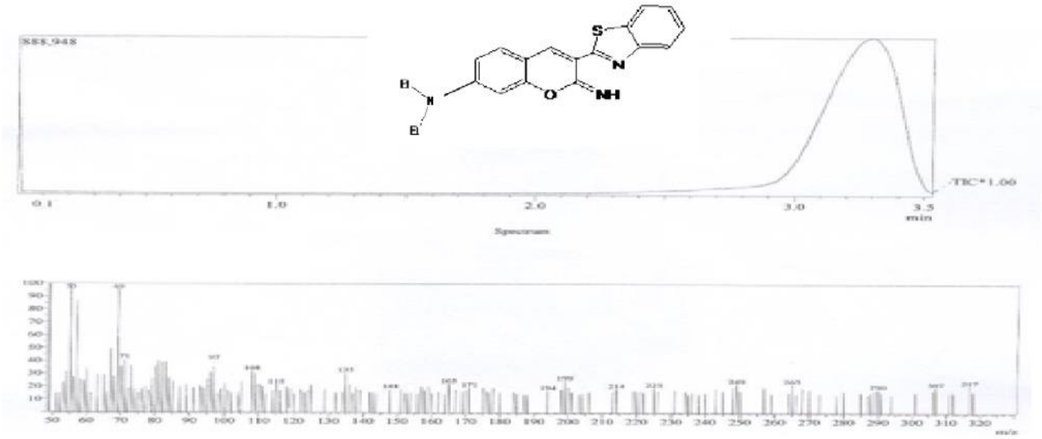


Figure (7): Mass Spectra of Synthesized 3b Dye.

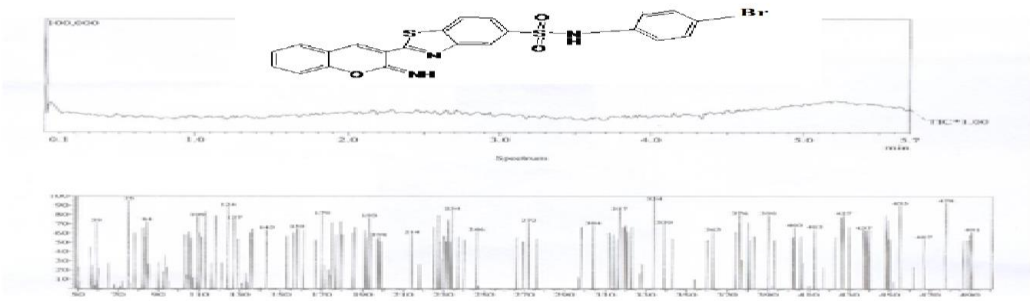


Figure (8): Mass Spectra of Synthesized 5a Dye.

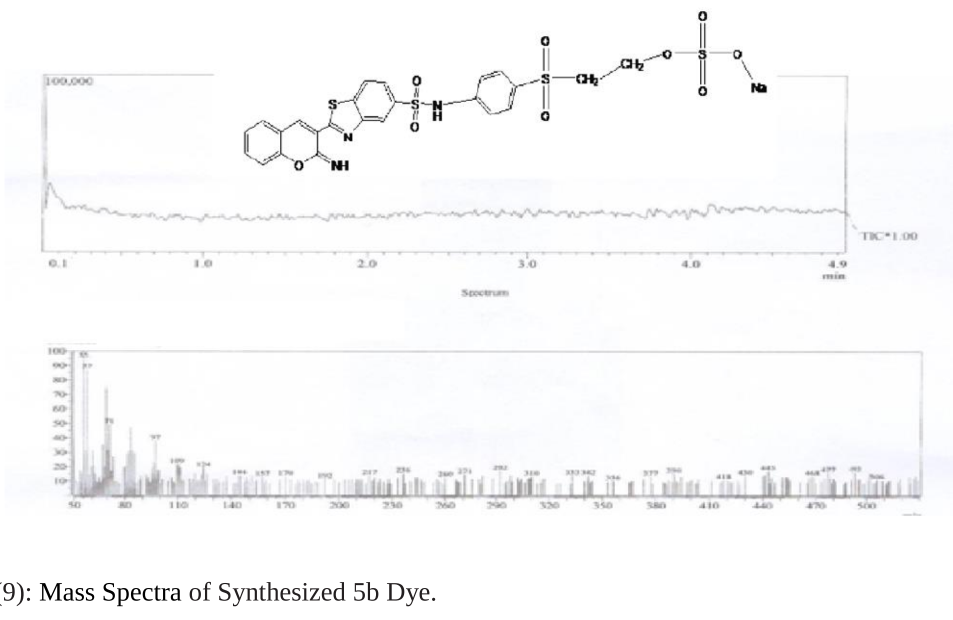


Figure (9): Mass Spectra of Synthesized 5b Dye.

Fluorescence Spectroscopy.

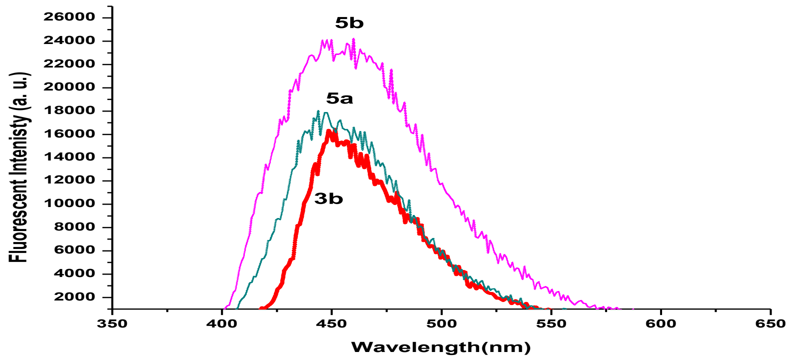


Figure (10): Fluorescence Spectra of 3_b and $5_{a\ and\ b}$ Dye.

The fluorescence spectra for the compounds (3_b and $5_{a\ and\ 3b}$) were measured upon the excitation at 390 nm and are shown in Figure 10. The fluorescence spectra of all dyes are similar in shape, position and the fluorescence intensity, there are two sharp emission peaks near 450 and 475 nm., and the highest emission peak arrange 5_b> 5_a>3b. The longer wavelength emission evidently give rise to difference in fluorescence peak position and intensity. A slightly red-shift fluorescent emission is spotted, owing to the larger conjugation of benzo-coumarin ring.

Utilization of the Prepared Fluorescent Dyes in Inkjet Printing:

Dynamic Viscosity (*η*):

The viscosity of the inks **(3b)** (encapsulated and surface modification) and $5_{a\ and\ b}$ (made from surface – modified pigments) were found to be 3.3, 7.8, 4.1 and 5 mPa s **(cP)** measured at 50 s^{-1} and 1.6, 5.2, 2.2 and 2.5 mPa s **(cP)** measured at 250 s^{-1} . We measure the viscosity, rate of share and sharing stress for one ink made from surface – modified pigments (5_b) at 50, 100, 150, 200 and 250 s^{-1} as shown in Table 5.

Table 5: The viscosity, Rate of Share and Sharing stress for (5_b) Ink at 50, 100, 150, 200 and 250 s^{-1}.

No. of Inter (S^{-1})	Rate of Share (S^{-1})	Sharing stress (d/Cm^2)	Viscosity (cP)
50	46.6	2.33	5
100	93	3.79	4.5
150	140	5.5	3.33
200	186	6.81	2.75
250	233	8.84	2.5

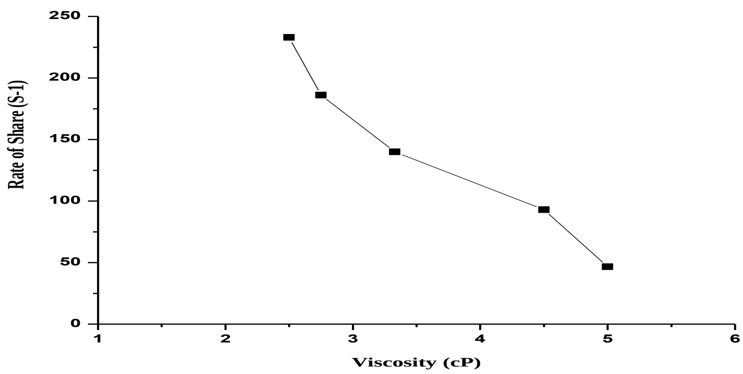


Figure (11): Plot of Rate of Share (S^{-1}) as a Function of Viscosity (cP) for Ink (5_b).

Luminescence of the printed samples under ultraviolet light

The printed paper and textile fabric samples were investigated by (VSC 6000) under ultraviolet light. The luminescence images of the printed Polyester, Polyamide and Paper of the three inks are shown in Figures 12, 13 and 14 respectively.

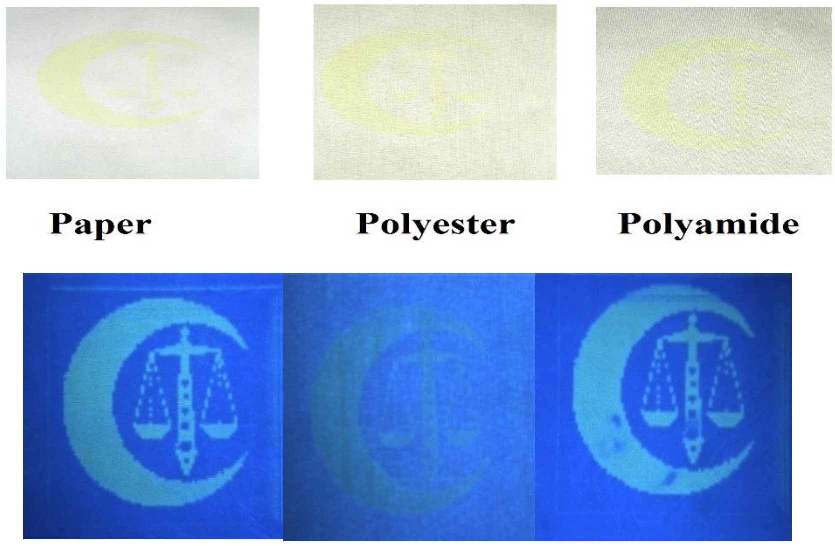


Figure (12): Luminescence Logo of the Printed dye 3b (Micro- encapsulation) without and under UV illumination (365 nm).

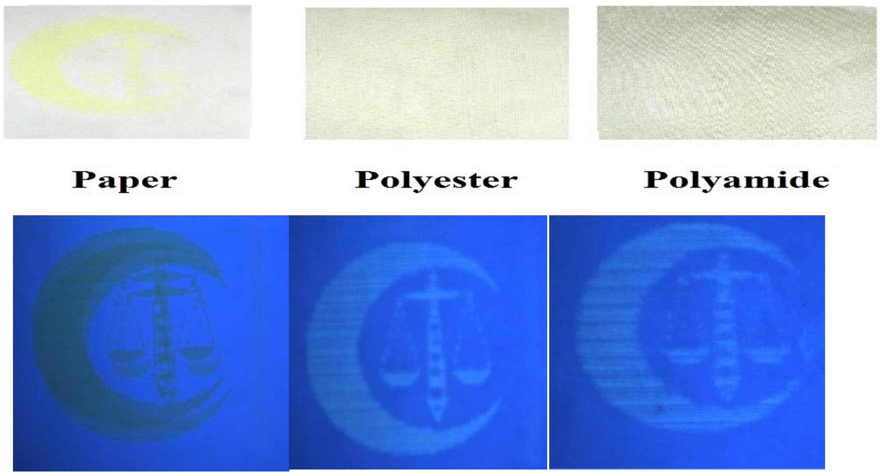
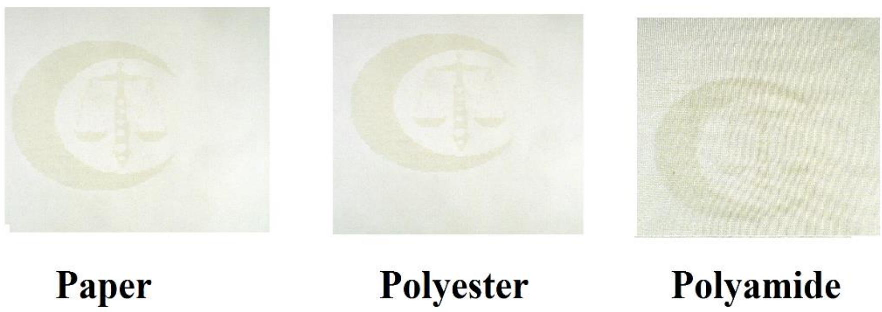


Figure (13): Luminescence Logo of the Printed dye 3b (Surface modified) without UV illumination and under UV illumination (365 nm).



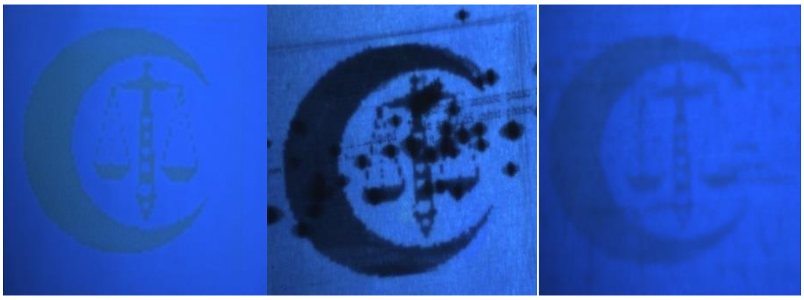


Figure (14): Luminescence Logo of the Printed dye 5_b (Surface modified) without UV illumination and under UV illumination (365 nm).

Fastness Properties and Color Strength:

Table 6 represented the fastness properties and color strength values of inkjet printed samples (paper, polyester and polyamide fabrics) using the newly prepared florescence inks (3b and 5_b) The data shows that excellent fastness to rubbing, washing and perspiration. The excellent fastness results indicate deeper penetration of ink in the substrate more than silk screen printing technique..

The small molecular size of ink has a significance effect on the rate of the dye out movement of the fabric during washing so, it is clear from Tables 6 that the washing fastness of the printed fabrics by surface modified inks (3b and 5b) are excellent but printed ones by microencapsulated ink (3b) indicate values 3-4 i.e. from good and not excellent due to the absence of binder.

The light fastness results (range from 4 to 6) depend on the groups attached to the coumarin or attached to the N-alkylsulfonamide group in case of 5_b dye.

Dye No.	K/S	Rubbing		Washing		Perspiration				Light fastness
						Alkali		Acid		
		Dry	Wet	Alt.	St.	Alt.	St.	Alt.	St.	
Polyester printed fabrics										
3b (Encapsulated)	13.9	4-5	4	4-5	4	4-5	4	4	4	4
3b (Surface Modified)	16.1	5	4-5	5	5	5	5	5	5	5
5_b	18.7	5-4	5	5	5	5	5	5	5	5-6
Polyamide printed fabrics										
3b (Encapsulated)	14.2	4	4	4-5	4	4-5	4	4	4	4
3b (Surface-Modified)	17.9	4-5	4-5	5	5	5-5	5	5	5	5
5_b	19.9	5	4-5	5	5	5	5	5	5	5-6

*Fixation temperature 190°C, Fixation time 2 min.

Table (7): Color Strength and Rubbing of Inkjet Printing Paper Using The Newly Synthesized Dyes (3b and 5_b):

ink No.	K/S	Rubbing	Light Fastness
3b (Encapsulated)	16.1	4-5	5-6
3b (Surface-Modified)	18.2	3-4	3-4
5_b	21.2	3-4	3-4

Table 7 indicate that the result of rubbing of paper printed by ink **(3b)** (by encapsulation), is values 4-5 due to the presence of polymer (PVA), but the result of rubbing of paper printed by surface modified inks **(3b)** and **(5_b),** indicate values 3-4 due to the absence of polymer (PVA).

Color strength:

Its clear from Figure 15 and 16. That the color strength (k/s) values of all printed fabrics increase with increasing the fixation temperature from 150°C to 190°C. It can be noticed also that, the ink (5_b) have highest (k/s) value and this may be due to chemical structure of the ink that has a good donating group (alkylsulfonamide groups attached to p-sulphatoethyl vinyl sulphone moiety) which leads to notable changes in the π-conjugated length and red-shifts in the absorption and emission spectra

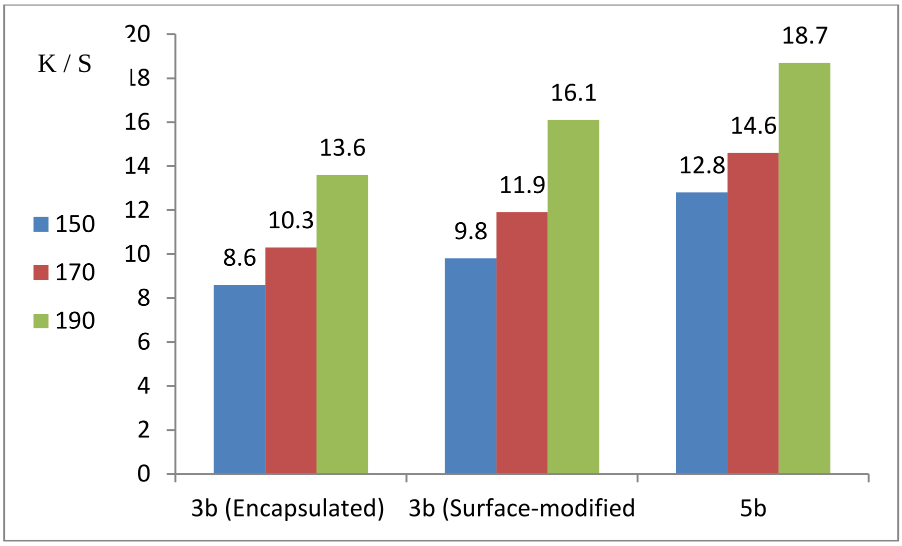


Figure (15): Effect of Inkjet Printing Temperature on The Color Strength of Inkjet Printed Polyester Fabric Using dyes 3b and 5_b, Fixation Time 2 min.

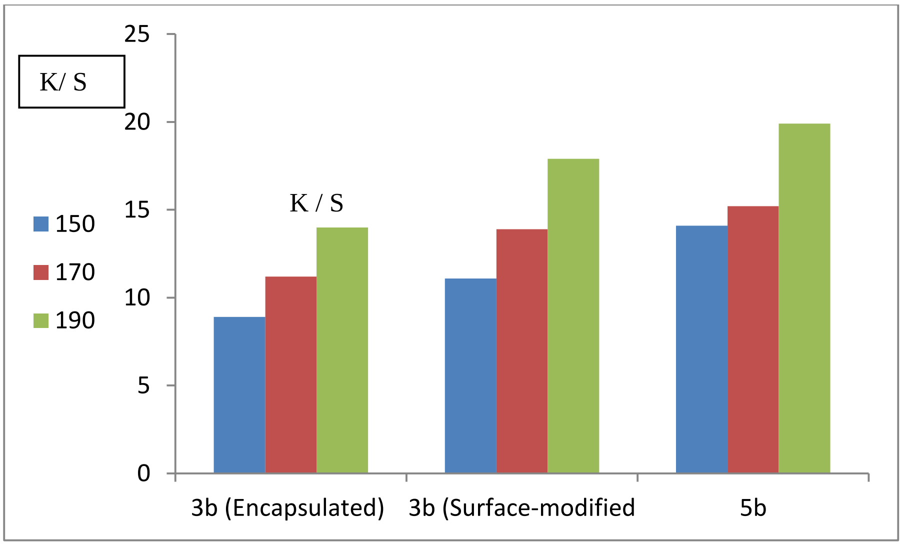


Figure (16): Effect of Inkjet Printing Temperature on The Color Strength of Inkjet Printed Polyamide Fabric Using dyes 3b and 5_b, Fixation Time 2 min.

Conclusion:

The synthesized inks are used in printing of polyester, polyamide fabrics and paper. The prints posse very good fastness properties and high fluorescence emission

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