Dec. 2016. Vol. 10. No. 01 ISSN2305-8269
International Journal of Engineering and Applied Sciences

www.eaas-journal.org

SYNTHETIC FIBER DYEING WITH SYNTHESIZED NOVEL DISPERSE DISAZO DYES CONTAINING METHYL (-CH_3) GROUP AS AN AUXOCHROME AND THEIR COLOR PROPERTIES

EMINE BAKAN[1], FİKRET KARCI[2], OZAN AVİNÇ[3]

[1] Department of Design, Higher Vocational School of Ulubey, Uşak University, Uşak, Turkey
[2] Department of Chemistry, Faculty of Science–Arts, Pamukkale University, Denizli, Turkey
[3]Department of Textile Engineering, Faculty of Engineering, Pamukkale University, Denizli, Turkey
[1]emine.tomruk@usak.edu.tr, [2]fkarci@pau.edu.tr, [3]oavinc@pau.edu.tr

ABSTRACT

Azo dyes constitute a very important class of organic compounds. These compounds are commonly used in different fields of industry due to their various prominent properties. One of the most well-known industries for these dyes is textile owing to dyeing characteristics of these dyestuffs. In this study, novel heterocyclic disazo disperse dyes, substituted with methyl (-CH_3) group at their o-, m-, p-position, synthesized and applied to poly (lactic acid), polyethylene terephthalate and polyamide 6.6 fibers. All applied synthesized disperse dyes resulted in yellow-red shades on studied fibers. Besides, the position of auxochrome group led to different colorimetric properties, color shades and exhaustion yields. Washing, perspiration, rubbing, sublimation, light, water, sea water fastness properties were generally in the commercially acceptable range. Overall, synthetic dyeing with novel heterocyclic disazo disperse dyes, substituted with methyl group (-CH_3) at their o-, m-, p-position, is applicable for textile industry in terms of color yields and fastness properties.

Keywords: ***Disperse dyes, color properties, exhaustion, fastness, methyl group, azo dye***

1. INTRODUCTION

As the chemical diversity of textile materials, dyestuffs uses for each are also different. According to fiber structure, depending on chemical structures (protein, cellulosic or synthetic based) within each textile material, different dyestuffs uses for coloring (Cegarra *et al.*, 1982). Especially disperse disazo dyestuffs uses for dyeing synthetic based fibers.

Disperse dyes, known as cellulose acetate dyes till 1934 are applied to hydrophobic fibers as aqueous suspensions today and is defined as dyestuffs that have too little water solubility. Disperse dyes can be applicable also to cellulose esters as applied for synthetic fibers as polyester, polyamide and acrylic. Today, only disperse dyes are used in polyester dyeing. More than %70 of the azo dyes are composed of disperse dyes.

The number of azo dyes, which constitute the most important class of organic dyes, is the sum of all other classes of dyes (Başer and İnanıcı, 1990). Because of the plurality of coloring power, able to be obtained easily from inexpensive starting materials, able to cover a very wide range of colors and show good fastness properties, azo dyes become more preferred in dyestuffs. Heterocyclic ring systems, used in the preparation of azo compounds, have an important place in dyeing industry (Shams *et al.*,2001; Elgemeie *et al.*,2003;Metwally *et al.*, 2012). Especially in recent years, heterocyclic azo compounds have become a new research area (Karapınar and Aksu, 2013; Karabacak *et al.*, 2015; Karcı and Bakan, 2015; Feng *et al*, 2016). For the purpose of getting brighter colors, polyfunctional heterocyclic systems have become interested. These dyestuffs are not only used for textile material dyeing, they are also used in antibiotic, antibacterial, antiviral, antifungal, antimicrobial, chemotherapeutic activities and as inhibitors in medical sector (Witherington *et al.*, 2003), (Yang *et al.*, 2009), (Farag *et al.*, 2010), (Kumar *et al.*, 2005), (Gudmundsson *et al.*, 2005), (Shams *et al.*, 2011), (Malladi *et al.*, 2013), (Shaki *et al.*, 2015), (Rizk *et al.*, 2015), Karabacak *et al.*, 2015.

In this study, we report the synthesis of 6 different pyrazole based disperse disazo dye

ISSN2305-8269
International Journal of Engineering and Applied Sciences

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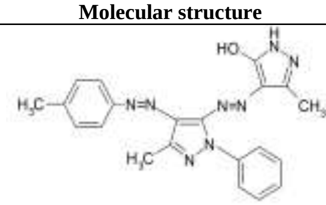
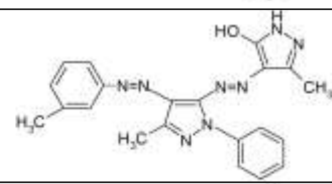
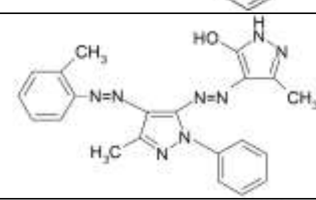
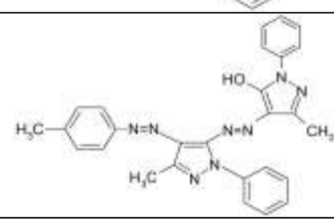
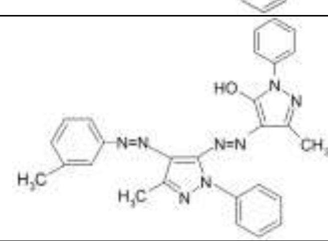
structure that have methyl (-CH_3) auxochrome group at their o-, m-, p-position. Then, these novel dyestuffs have applied to 3 different synthetic fibers at certain dyeing conditions. The exhaustion parameter during dyeing process examined and color properties are also compared in detail. Fastness properties of the synthetic fibers are evaluated too.

2. MATERIAL AND METHODS

100% PLA (30/1 Ne staple yarn), 100% PET (30/1 Ne staple yarn) and 100% Polyamide 6.6 (78 dtex/68 filament yarn/ two folded) fibers used for evaluation. Six different heterocyclic disperse disazo dyes as shown in Table 1 are used. The chemicals, used for the synthesis of the compounds, were obtained from Aldrich and Merck without further purification. The solvents used were of spectroscopic grade (Karcı and Bakan, 2015). Elemental analysis was carried out using a Leco CHNS-932 analyzer. Ultraviolet–visible (UV–vis) absorption spectra were recorded via a Schimadzu UV-1601 double beam spectrophotometer at the wavelength of maximum absorption (λmax) in a range of different solvents, i.e. DMSO, DMF, acetonitrile, methanol, acetic acid and chloroform at various concentrations ($1 \times 10^{-6} - 10^{-8}$). IR spectra were determined via Mattson 1000 Fourier Transform infrared (FT-IR) spectrophotometer using a KBr disc. Nuclear magnetic resonance (^{1}HNMR) spectra were recorded on a Bruker-Spectrospin Avance DPX 400 Ultra-Shield in dimethylsulphoxide (DMSO) using tetramethylsilane (TMS) as the internal reference and chemical shifts (δ) were given in ppm. Melting points were determined on an Electro thermal 9100 melting point apparatus and are uncorrected.

Code	Generic Name	Position of -CH_3 group	Molecular structure
3a	4-(4′-(p-methylphenylazo)-3′-methyl-1′-phenylpyrazole-5′-ylazo)-5-hydroxy-3-methyl-1H-pyrazole	Para	
3b	4-(4′-(m-methylphenylazo)-3′-methyl-1′-phenylpyrazole-5′-ylazo)-5-hydroxy-3-methyl-1H-pyrazole	Meta	
3c	4-(4′-(o-methylphenylazo)-3′-methyl-1′-phenylpyrazole-5′-ylazo)-5-hydroxy-3-methyl-1H-pyrazole	Ortho	
4a	4-(4′-(p-methylphenylazo)-3′-methyl-1′-phenylpyrazole-5′-ylazo)-5-hydroxy-3-methyl-1-phenylpyrazole	Para	
4b	4-(4′-(m-methylphenylazo)-3′-methyl-1′-phenylpyrazole-5′-ylazo)-5-hydroxy-3-methyl-1-phenylpyrazole	Meta	

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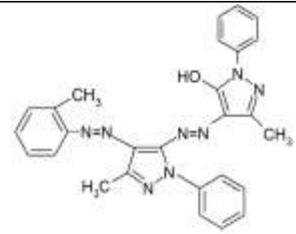
4c	4-(4′-(o-methylphenylazo)-3′-methyl-1′-phenylpyrazole-5′-ylazo)-5-hydroxy-3-methyl-1-phenylpyrazole	Ortho	

Table 1: Molecular structures of synthesized heterocyclic disperse dyes

Six dyes, $-CH_3$ auxochrome group on para, meta and ortho positions, were applied to PLA, PET and PA 6.6 fiber fabrics. Dyeing were carried out at a laboratory type ATAÇ LAB-DYE HT Infra-red dyeing machine at a liquor ratio of 30:1 and 2% owf (on weight fabric). Dyeing procedures are shown on Figure 1. Dyeing conditions were chosen according to the literature and commercial scale application information from the industry in order to achieve best available dyeing performance without giving any damage to respected fibers (Avinc *et al.*, 2010; Avinç *et al.*, 2012). For example, the dyeing temperature for PLA was used in accordance with the recommendations outlined by DyStar (2004). Subsequent to dyeing, reductive clearing process was carried out with 2 g/l Na_2CO_3 and 2 g/l $Na_2S_2O_4$ at 40°C for 15 minutes. Finally, cold rinsing was carried out.

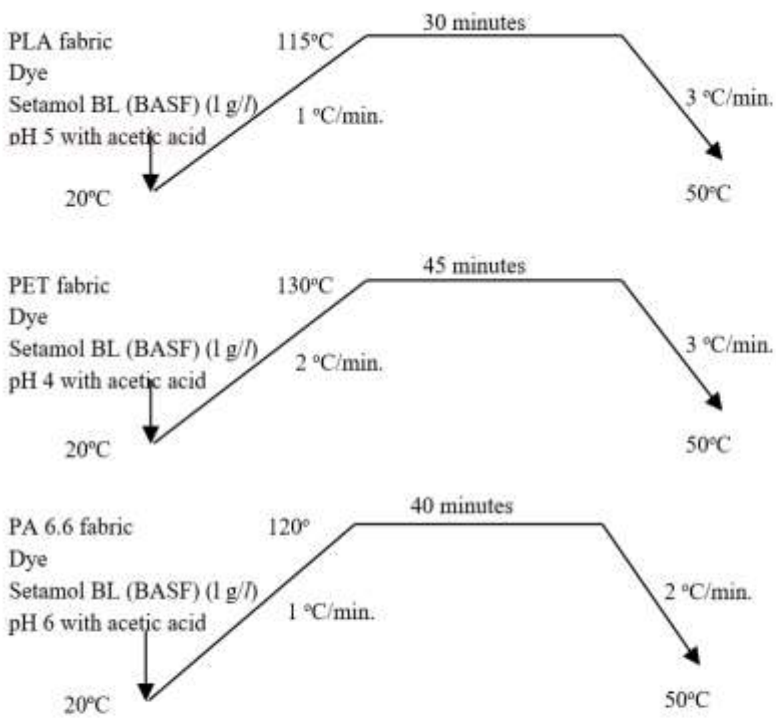


Figure 1: *Disperse dyeing procedures used for synthetic fibers*

2.1 DETERMINATION OF EXHAUSTION YIELDS

Dye exhaustion was determined by UV spectrophotometer (Perkin Elmer) which measures the absorbance at the wavelength of maximum absorption (λmax). The dye uptake was calculated by following equation:

$$\%E = ((Ao-A1)/ Ao) \times 100$$

In which; Ao and A_1 are the absorbance values of dye liquors at λmax before and after dyeing operation, respectively.

ISSN2305-8269
International Journal of Engineering and Applied Sciences

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2.2COLOR PROPERTIES MEASUREMENT

CIELAB color properties of the samples were determined with Datacolor 600 spectrophotometer under D65 standard day light (10^o observer). *K/S* color strength values were calculated according to Kubelka - Munk equation.

2.3 FASTNESS TESTS

- Washing fastness were performed according to ISO 105 C06 A2S for PA 6.6, ISO 105 C06 B2S for PLA and PET.
- Both alkaline and acid perspiration fastness were determined according to the ISO 105-E04 protocol.
- Wet & dry rub fastness tests were performed according to ISO 105 X12 standard.
- Sublimation fastness tests were performed following ISO 105: P01 protocol using SDL Scorch Tester M247B at 180^{o}C for 30 seconds for PET and PA 6.6 fiber fabrics (for even comparison) and lower temperature of 130^{o}C for 30 seconds in the case of PLA fiber fabrics.
- The assessment of water fastness and sea water fastness tests were performed according to the ISO 105-E01 and ISO 105-E02 respectively.

All fastness except light fastness were evaluated via using ISO grey scale. Light fastness testing was carried out according to ISO 105: B02. Color fastness to light was evaluated using the blue wool scale.

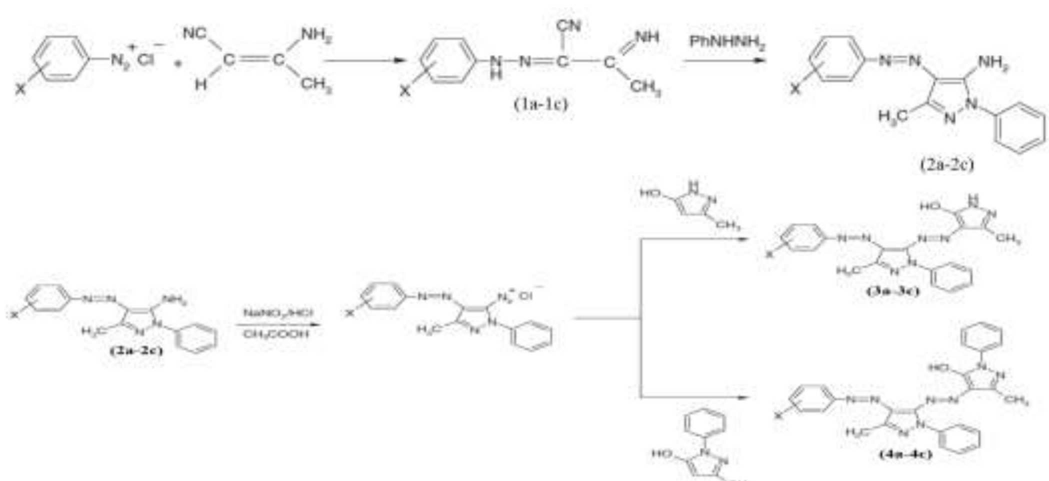
3. RESULTS AND DISCUSSION

3.1 SYNTHESIS CHARACTERIZATION OF HETEROCYCLIC DISAZO DYES

2-Arylhydrazone-3-ketiminobutyronitriles (1a–1c) and 5-amino-4-arylazo-3-methyl-1-phenylpyrazoles (2a–2c) were prepared according to the literature procedures (Karcı, 2005; Elnagdi *et al.*, 1976; Elnagdi *et al.*, 1985). The general route for the synthesis of 2-arylhydrazono-3-ketiminobutyronitriles and 5-amino-4-arylazo-3-methyl-1-phenylpyrazoles is outlined in Scheme 1.

5-Amino-4-arylazo-3-methyl-1-phenylpyrazoles (0.01 mol) were dissolved in a mixture of glacial acetic acid and concentrated hydrochloric acid (20 ml, ratio 1:1) and the solution was then cooled to 0–5 °C. Sodium nitrite (0.69 g, 0.01 mol) in water (10 ml) was then added to this solution drop wise with vigorous stirring, for about 1 h, while cooling at 0–5 °C. Then the resulting diazonium solution was added in portions over 30 min to a vigorously stirred solution of 5-hydroxy-3-methyl-1H-pyrazole or 5-hydroxy-3-methyl-1-phenylpyrazole (0.01 mol) in KOH (0.56 g, 0.01mol) and water (10ml) between 0 and 5 °C, maintaining the pH at 7–8 by simultaneous sodium acetate solution addition. The mixture was then stirred for 2 h at 0–5 °C. The precipitated product separated upon dilution with water (50 ml) was filtered off, washed with water several times, dried and crystallized from DMF–H_2O (Scheme 1).

All synthesized dyes were characterized by elemental analysis and spectral methods (Tables 2-4). The effect of solvent upon the absorption ability of dyes substituted with methyl group at their o-, m-, p-position was examined in detail (Table 5).



Scheme 1: *Synthesis of heterocyclic disazo dyestuffs (X: -CH_3)*

Code	Molecular Formula	Molecular Weight (gr/mol)	Melting Point (^{0}C)	Elemental Analysis					
				C (%)		H(%)		N(%)	
				Calculated	Found	Calculated	Found	Calculated	Found
3a	$C_{21}H_{20}N_8O$	400	90-91	62.99	62.90	5.03	4.90	27.98	27.91
3b	$C_{21}H_{20}N_8O$	400	230-231	62,99	63,15	5,03	5,12	27,98	28,21
3c	$C_{21}H_{20}N_8O$	400	180-181	62,99	63,23	5,03	4,95	27,98	28,05
4a	$C_{27}H_{24}N_8O$	476	259-260	68,05	68,14	5,08	5,32	23,51	23,65
4b	$C_{27}H_{24}N_8O$	476	230-231	68,05	68,11	5,08	5,22	23,51	23,70
4c	$C_{27}H_{24}N_8O$	476	241-242	68,05	67,92	5,08	4,87	23,51	23,45

***Table 2**: Elemental analyses of synthesized heterocyclic disperse dyes and melting points*

Code	FT-IR (cm^{-1}, in KBr)				
	ν_{NH}	ν_{Aro-H}	ν_{Alip-H}	$\nu_{C=O}$	$\nu_{N=N}$
3a	3188	3047	2916	1666	1536
3b	3170	3064	2919	1659	1497
3c	3149	3064	2979	1663	1500
4a	3191	3025	2919	1659	1504
4b	3131	3054	2916	1666	1532
4c	3195	3061	2923	1666	1539

***Table 3**: FT-IR analyses of synthesized heterocyclic disperse dyes*

Code	^{1}H-NMR (δ, ppm, DMSO-d$_6$)		
	Aliphatic - H	Aromatic - H	X-H
3a	2,28 (s, 3H, CH_3) 2,67 (s, 3H, CH_3) 2,38 (s, 3H, p-CH_3)	7,16-8,03 (m, 9H)	11,71 (g, -OH) 13,30 (g, -NH) 14,17 (g, -NH hidrazo)
3b	2,29 (s, 3H, CH_3) 2,72 (s, 3H, CH_3) 2,41 (s, 3H, m-CH_3)	7,04-7,95 (m, 9H)	11,74 (g, -OH) 13,16 (g, -NH) 14,15 (g, -NH hidrazo)
3c	2,30 (s, 3H, CH_3) 2,72 (s, 3H, CH_3) 2,36 (s, 3H, o-CH_3)	7,30-7,93 (m, 9H)	11,65 (g, -NH) 13,78 (g, -NH hidrazo)
4a	2,30 (s, 3H, CH_3) 2,72 (s, 3H, CH_3) 2,39 (s, 3H, p-CH_3)	7,20-8,09 (m, 14H)	12,20 (g, -OH) 13,30 (g, -NH) 14,21 (g, -NH hidrazo)
4b	2,30 (s, 3H, CH_3) 2,74 (s, 3H, CH_3) 2,37 (s, 3H, m-CH_3)	7,06-8,46 (m, 14H)	13,29 (g, -NH) 14,34 (g, -NH hidrazo)
4c	2,27 (s, 3H, CH_3) 2,73 (s, 3H, CH_3) 2,36 (s, 3H, o-CH_3)	7,23-7,87 (m, 14H)	13,85 (g, -NH hidrazo)

***Table 4**: ^{1}H-NMR analyses of synthesized heterocyclic disperse dyes*

Code	DMSO	DMF	Acetonitrile	Methanol	Acetic Acid	Chloroform
3a	397 346	402 345	394 342	398 339	401 340	402 344
3b	391 347	394 345	387 341	394 337	394 339	397 345
3c	395 340	406 340	399 338	392 337	406 333	409 340
4a	422 345	423 344	411 341	398 340	409 341	416 344
4b	418 343	420 341	411 339	401 337	415 336	415 341
4c	410 338	413 337	405 334	409 333	408 332	408 338

***Table 5**: λmax(nm) values of synthesized heterocyclic disperse dyes in different solvents*

Dec. 2016. Vol. 10. No. 01 ISSN2305-8269
International Journal of Engineering and Applied Sciences

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3.2 COLOR PROPERTIES AND EXHAUSTION YIELDS

Colorimetric properties of PLA, PET and PA 6.6 fiber fabric samples dyed with the novel synthesized disperse dyes were shown on Table 6 and Figure 2. Since molecular weight (Table 2) of 3a-3c dyes are lower, exhaustion and color yields of 3a-3c dyes are higher than 4a-4c dyes. It can also be seen from molecular structures, Table 1.

Difference between the dyes resulted from the position of the methyl group which directly affects the characteristics of the dye molecule. Among all dyestuffs, color yields (*K/S*) of PLA fabric dyed with 3b has the darkest shade respectively. In addition, 3b and 4b dyestuffs have the higher values among PLA, PET and PA 6.6 separately.

As it is understood from Table 6, the result of dyeing PLA, PET and PA 6.6 with 6 different dye, a* and b* values showed that fabrics color shades are between yellow-orange and red. In other words, hue angle value (h^0 value) is below 90^0 and supports that all samples color shades are at the axis of a*-b* and between yellow and red shades. Figure 2 shows that as a result of dyeing PLA, PET and PA 6.6 with 3a-3c and 4a-4c dyes, fabrics color shades are at the +a and +b axis.

When the color saturation (Chroma, C*) of dyes is considered, it is seen that saturation at the dyes for 3a-3c has higher than 4a-4c. In addition, all colorimetric values of PA 6.6 fiber fabrics are lower than the other fabrics; PLA and PET. It can be said from Figure 2 that, color saturation (C*) of the dyes are lower than PET and PLA fabrics comparably. This case proves the lowest color yield (K/S) value as the reason of lower color saturations.

PLA fabric, dyed with 4a dyestuff containing p-CH_3 substituent group, showed the darkest color shades (L*).

Fabric	Dyestuff	*K/S*	Exhaustion (%)	h^0	C*	L*
PLA	3a	27,2	94,69	83,3	86,6	76,4
	3b	28,8	93,34	79,5	82,0	72,8
	3c	11,5	97,95	82,5	74,0	77,8
PET	3a	21,5	97,75	78,4	88,6	74,7
	3b	22,9	92,36	75,6	87,5	71,8
	3c	18,8	81,17	78,5	84,7	72,9
PA 6.6	3a	10,6	88,05	83,8	68,2	75,4
	3b	13,2	85,20	75,5	66,7	68,1
	3c	7,32	92,60	81,0	60,2	72,8
PLA	4a	3,80	89,79	88,8	56,3	84,4
	4b	7,89	83,03	78,6	74,5	78,7
	4c	1,75	82,28	83,4	45,7	83,2
PET	4a	5,08	79,5	80,6	64,6	80,7
	4b	8,31	84,24	75,7	71,8	76,0
	4c	2,46	67,13	79,1	50,0	79,9
PA 6.6	4a	3,17	86,91	85,5	53,0	80,3
	4b	5,14	76,05	78,6	61,9	76,1
	4c	1,89	90,76	85,4	45,5	82,1

Table 6: *Percentage exhaustion and color properties of dyed samples*

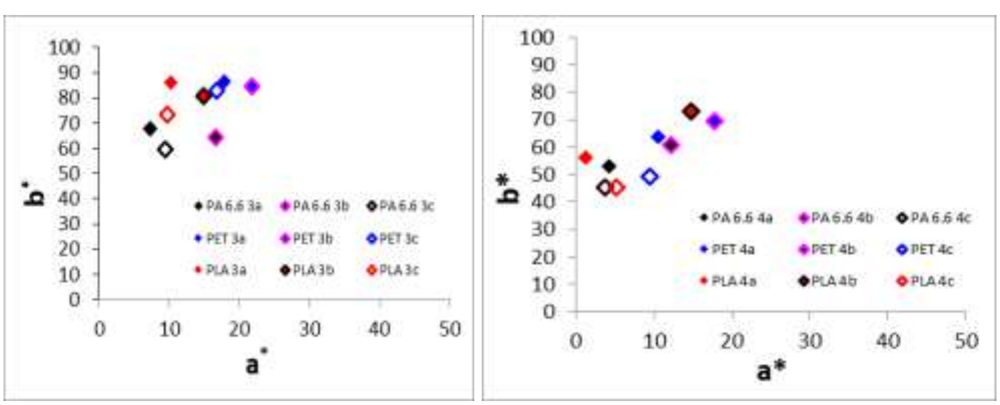

Figure 2: *a* and b* values of dyed samples (3a-3c left, 4a-4c right)*

Dec. 2016. Vol. 10. No. 01 ISSN2305-8269
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3.3 FASTNESS PERFORMANCE

Wash (shade change and staining), perspiration (acidic and alkaline), rub (wet and dry), sublimation, light, water and sea water fastness properties were examined for all fibers studied.

The wash fastness staining and shade change values of PLA, PET and PA 6.6 samples dyed with 3a-3c and 4a-4c dyes were in the commercially acceptable range (between 4-5) according to gray scale ratings (Table 7).

Fabric	Dyestuff	*Shade Change*	Multifiber Staining(ISO 105 C06/B2S for PLA and PET) ISO 105 C06/A2S for PA 6.6)					
			Wool	Acrylic	Polyester	Polyamide	Cotton	Acetate
PLA	3a	4/5-5	4/5	4/5-5	4/5	4	4/5	4
	3b	4/5-5	4/5-5	4/5-5	4/5	4-4/5	4/5	4-4/5
	3c	4/5-5	4/5-5	5	5	4/5-5	5	4/5-5
	4a	4/5-5	5	5	5	4/5-5	5	5
	4b	4/5-5	5	5	5	4/5-5	5	5
	4c	4/5-5	5	5	5	4/5-5	5	5
PET	3a	5	5	5	5	4/5-5	5	5
	3b	5	5	5	5	5	5	5
	3c	5	5	5	5	4/5-5	5	5
	4a	5	5	5	5	5	5	5
	4b	5	5	5	5	5	5	5
	4c	5	5	5	5	5	5	5
PA 6.6	3a	5	4/5	5	4/5	4-4/5	4/5	4
	3b	4-4/5	4/5	5	4/5	4	4/5	4
	3c	4/5	4/5-5	5	5	4/5	5	4/5
	4a	4/5	5	5	5	4/5	5	4/5
	4b	4	5	5	4/5	4	4/5-5	4
	4c	4/5	5	5	4/5-5	4-4/5	4/5-5	4-4/5

Table 7: *Wash fastness values of PLA, PET and PA 6.6 fiber fabrics dyed with 3a-3c and 4a-4c dyes*

Dry and wet rub fastness values of dyed PLA, PET and PA 6.6 fiber fabrics were in the commercially acceptable range (between 3/4-5) according to gray scale. Especially all dyes (3a-3c and 4a-4c) exhibited excellent wet rubbing fastness performance on PET fabric with no staining. However, all these rubbing fastness results are good and commercially acceptable (Table 8).

Fabric	Dye	Rub Fastness (ISO 105: X12) (Cotton Staining)		Fabric	Dye	Rub Fastness (ISO 105: X12) (Cotton Staining)		Fabric	Dye	Rub Fastness (ISO 105: X12) (Cotton Staining)	
		Dry	Wet			Dry	Wet			Dry	Wet
PLA	3a	4	4/5	PET	3a	4/5-5	5	PA 6.6	3a	5	5
	3b	3/4-4	4/5		3b	5	5		3b	4/5-5	4/5-5
	3c	4-4/5	4/5		3c	5	5		3c	4/5-5	4/5
	4a	4	4/5-5		4a	4/5-5	4/5-5		4a	5	4/5-5

4b	3	4-4/5	**4b**	4/5	4/5-5	**4b**	4/5	4/5
4c	4-4/5	4/5	**4c**	5	5	**4c**	5	5

Table 8: *Dry and wet rub fastness of PLA, PET and PA 6.6 fiber fabrics dyed with 3a-3c and 4a-4c dyes*

The alkaline (Table 9) and acidic (Table 10) perspiration fastness values of dyed PLA, PET and PA 6.6 fiber fabrics were in the commercially acceptable range (between 4-5) according to gray scale. Especially PLA and PET fibers not only alkaline perspiration fastness values but also acidic perspiration fastness values were perfect and all staining values were 5 at gray scale. On the other hand, PA 6.6 fiber fabrics both alkaline and acidic perspiration values staining on Polyamide, Cotton and Acetate adjacent multifiber stripe slightly worse than PLA and PET fiber fabrics.

Fabric	Dyestuff	Multifiber staining (ISO 105 - E04), Alkaline					
		Wool	Acrylic	Polyester	Polyamide	Cotton	Acetate
PLA	3a	5	5	5	5	5	5
	3b	5	5	5	5	5	5
	3c	5	5	5	5	5	5
	4a	5	5	5	5	5	5
	4b	5	5	5	5	5	5
	4c	5	5	5	5	5	5
PET	3a	5	5	5	5	5	5
	3b	5	5	5	5	5	5
	3c	5	5	5	5	5	5
	4a	5	5	5	5	5	5
	4b	5	5	5	5	5	5
	4c	5	5	5	5	5	5
PA 6.6	3a	5	5	5	4/5-5	4/5-5	4/5-5
	3b	5	5	5	4/5	5	4/5-5
	3c	5	5	5	4/5-5	5	4/5-5
	4a	5	5	5	4/5-5	5	4/5-5
	4b	5	5	5	4/5-5	5	4/5-5
	4c	5	5	5	4/5-5	5	4/5-5

Table 9: *Alkaline perspiration fastness of PLA, PET and PA 6.6 fiber fabrics dyed with 3a-3c and 4a-4c dyes*

Fabric	Dyestuff	Multifiber staining (ISO 105 - E04), Acidic					
		Wool	Acrylic	Polyester	Polyamide	Cotton	Acetate
PLA	3a	5	5	5	5	5	5
	3b	5	5	5	5	5	5
	3c	5	5	5	5	5	5
	4a	5	5	5	5	5	5
	4b	5	5	5	5	5	5
	4c	5	5	5	5	5	5
PET	3a	5	5	5	5	5	5
	3b	5	5	5	5	5	5

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	3c	5	5	5	5	5	5
	4a	5	5	5	5	5	5
	4b	5	5	5	5	5	5
	4c	5	5	5	5	5	5
PA 6.6	3a	5	5	5	4/5	4/5-5	4/5
	3b	5	5	5	4/5	4/5	4/5
	3c	5	5	5	4/5	5	4/5-5
	4a	5	5	5	4/5-5	5	4/5-5
	4b	5	5	5	4/5-5	5	4/5-5
	4c	5	5	5	4/5-5	5	4/5-5

Table 10: *Acidic perspiration fastness of PLA, PET and PA 6.6 fiber fabrics dyed with 3a-3c and 4a-4c dyes*

The staining sublimation fastness properties of synthesized dyes (3a-3c and 4a-4c) exhibited moderate (3) to very good (5) results. Especially PLA fabrics had the better values on the adjacent multifiber stripe than PET and PA 6.6. PET exhibited slightly worse staining than PLA and PA 6.6. However, shade change sublimation fastness performances for all fabrics were very good (Table 11).

Fabric	Dye	*K/S*	*Shade Change*	Multifiber staining (ISO 105: P01)					
				Wool	Acrylic	Polyester	Polyamide	Cotton	Acetate
PLA	3a	27,2	5	4/5	5	4	4	4/5	4/5
	3b	28,8	5	4/5	5	4	4	5	4/5
	3c	11,5	4/5-5	5	5	4/5	4/5	5	5
	4a	3,80	5	5	5	5	5	5	5
	4b	7,89	5	5	5	5	5	5	5
	4c	1,75	4/5-5	5	5	5	5	5	5
PET	3a	21,5	5	3/4	4/5	2/3	3	4	3/4
	3b	22,9	5	3/4	4	2/3	2/3	4	3/4
	3c	18,8	5	4	4/5	3	3/4	4/5	4
	4a	5,08	5	4/5	5	4	4/5	5	4/5
	4b	8,31	5	4/5	5	4	4/5	5	4/5
	4c	2,46	4/5-5	5	5	5	5	5	5
PA 6.6	3a	10,6	5	3/4	4/5	2	2/3	4	3/4
	3b	13,2	4/5-5	3/4	4	3	3	4	3/4
	3c	7,32	5	4	4/5	3	3/4	4/5	4
	4a	3,17	5	4/5	5	3/4	4	5	4/5
	4b	5,14	5	4/5	5	3/4	4	5	4/5
	4c	1,89	5	4/5	5	4/5	5	5	5

Table 11: *Sublimation fastness of PLA, PET and PA 6.6 fiber fabrics dyed with 3a-3c and 4a-4c dyes*

Light fastness performance was quite high for PET samples by comparison to PLA and PA 6.6 fiber fabrics according to blue scale rating. Because of the lower color yield (K/S) of PA 6.6, their light fastness performance gave also lower results compared with PLA and PET fabrics (Table 12).

Dyestuff	PLA *K/S*	PLA Light fastness (Xenon) (ISO 105: B02)	PET *K/S*	PET Light fastness (Xenon) (ISO 105: B02)	PA 6.6 *K/S*	PA 6.6 Light fastness (Xenon) (ISO 105: B02)
3a	27.2	4	21.5	5	10.6	3
3b	28.8	4	22.9	6	13.2	4
3c	11.5	5	18.8	6	7.32	3
4a	3,80	4	5,08	5	3,17	4
4b	7,89	5	8,31	6	5,14	4
4c	1,75	4	2,46	5	1,89	3

Table 12: *Light fastness of PLA, PET and PA 6.6 fiber fabrics dyed with 3a-3c and 4a-4c dyes*

Water fastness and sea water fastness performances of all fabrics were excellent and all staining values were 5 at gray scale for PLA and PET fiber fabrics (Table 13). On the other hand, PA 6.6 fiber fabrics staining on Polyamide, Cotton and Acetate adjacent multifiber stripe slightly had 4/5 gray scale values.

Fabric	Dye	Water Fastness (ISO 105-E01) Wool	Acrylic	Polyester	Polyamide	Cotton	Acetate	Sea Water Fastness (ISO 105-E02) Wool	Acrylic	Polyester	Polyamide	Cotton	Acetate
PLA	3a	5	5	5	5	5	5	5	5	5	5	5	5
	3b	5	5	5	5	5	5	5	5	5	5	5	5
	3c	5	5	5	5	5	5	5	5	5	5	5	5
	4a	5	5	5	5	5	5	5	5	5	5	5	5
	4b	5	5	5	5	5	5	5	5	5	5	5	5
	4c	5	5	5	5	5	5	5	5	5	5	5	5
PET	3a	5	5	5	5	5	5	5	5	5	5	5	5
	3b	5	5	5	5	5	5	5	5	5	5	5	5
	3c	5	5	5	5	5	5	5	5	5	5	5	5
	4a	5	5	5	5	5	5	5	5	5	5	5	5
	4b	5	5	5	5	5	5	5	5	5	5	5	5
	4c	5	5	5	5	5	5	5	5	5	5	5	5
PA 6.6	3a	5	5	5	4/5	5	4/5	5	5	5	4/5-5	5	5
	3b	5	5	5	4/5	5	5	5	5	5	4/5-5	5	5
	3c	5	5	5	5	5	5	5	5	5	5	5	5
	4a	5	5	5	5	5	5	5	5	5	5	5	5
	4b	5	5	5	5	5	5	5	5	5	5	5	5
	4c	5	5	5	5	5	5	5	5	5	5	5	5

Table 13: *Water and sea water fastness of PLA, PET and PA 6.6 fiber fabrics dyed with 3a-3c and 4a-4c dyes*

4. CONCLUSION

6 different disperse disazo dyes were synthesized and applied to PLA, PET and PA 6.6 fiber fabrics respectively. Colorimetric properties, exhaustion yields and fastness parameters were evaluated and compared.

Yellow and orange shades (According to axis of a*-b*) were obtained on PLA, PET and PA 6.6 fibers by 2% application of 3a, 3b, 3c, 4a, 4b and 4c dyestuffs. Mostly darker shades obtained from 3a, 3b and 3c dyestuffs (*K/S* >10) and medium dark shades obtained from 4a, 4b and 4c dyestuffs (*K/S* <10) for all fiber fabrics. Exhaustion and color yields of 3a-3c dyes were

higher than 4a-4c dyes according to their molecular weight respectively.
Difference between the dyes resulted from the position of the methyl group, directly affected the characteristics of the dye molecule. Among all dyestuffs, color yields (*K/S*) of PLA, PET and PA 6.6 fabrics dyed with 3b and 4b dyes which had meta methyl auxochrome had the darkest shade compared to the dyes that had ortho and para methyl auxochromes. The color saturation (Chroma, C*) of 3a-3c dyes were higher than 4a-4c dyes respectively. PLA fabric, dyed with 4a dyestuff containing p-CH_3 substituent group, showed the darkest color shades (L*).
Actually all exhaustion yields of dyes were higher than 76%. Only the exhaustion value of PET fiber fabric dyed with 4c had 67% yield.
Washing, perspiration, rubbing, sublimation, light, water, sea water fastness values were generally in the commercially acceptable range. Overall, PLA, PET and PA 6.6 dyeing with 3a, 3b, 3c, 4a, 4b and 4c dyestuffs is applicable for textile industry in terms of color yields and fastness properties.

Acknowledgements
This study is sponsored and supported by Pamukkale University Scientific Research Project Coordination Unit PAUBAP by the project number of 2012FBE035.

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