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Synthesis and Application of Functional (Anti-UV) Azo-dyes based on γ-acid on Wool Fabrics

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Abstract

Several azo acid dyes with built-in UV-absorber residues (resorcinol, 2, 4- dihydroxy benzophenone, 1- hydroxy benzotriazol sulfonic acid) were synthesised. The structure of the synthesized dyes was fully elucidated by using FTIR, ^{1}H-NMR.

In this paper we report the synthesis and application of the anti-UV dyes on wool fabrics aiming to these new dyes might reduce the undesirable photo – degradation effects of UVR on dyed fabrics and also to prevent UVR reaching the human skin which causes cell damage and skin cancer.

Fabrics dyed with anti-UV dyes were tested for color strength (K/S), rate of fading (ΔE) values and fastness properties.

Keywords: Azo Dyes, Characterization, Color Strength (K/S), Dyeing, Synthesis, UV Absorbers, Wool Fabric

1. Introduction

In the last decade increasing attention has been paid to protective properties of textiles against UV radiation originating from sunlight1. Protection against strong solar radiation is usually afforded by applying a composition that contains a UV absorber (sunscreen) directly to the skin. The safest protection from UV radiation (UVR) exposure is also offered by clothing and its protectiveness depends on fabric composition (natural, artificial or synthetic fibers), fabric parameters (porosity, weight and thickness) and dyeing (natural or synthetic dyes, dye concentration, UV absorbing properties, etc.)[1].

In recent reviews of the possible development of synthetic dyes for textile applications, it has been suggested that a modern colorant could also perform additional functions such as antibacterial action, increased UV- or IR- absorption, or water repellence[2,3]. These dual dye properties would allow the number of chemicals used in the dyehouse to be reduced.

The present study is an attempt to synthesis several azo acid dyes with built-in UV-absorber residues to obtain functional anti-UV dyes.

UV absorbers are organic or inorganic colourless compounds with strong absorption in the UV range of 290–360 nm[4–17].

UV absorbers incorporated into the fibres convert electronic excitation energy into thermal energy, function as radical scavengers and singlet oxygen quenchers. The high-energy, short-wave UVR excites the UV absorber to a higher energy state; the energy absorbed may then be dissipated as longer-wave radiation[18]. Alternately, isomerisation can occur and the UV absorber may then fragment into non-absorbing isomers[7].

Author for correspondence

2. Experimental

2.1 Materials

2.1.1 Substrate

Wool fabric 310 g/m^2 was supplied by Golden Tex Co., Tenth of Ramadan-Egypt, initially was treated with a solution containing 0.5 g/L sodium carbonate and 2 g/L nonionic detergent at 60°C for 30 min, after which time it was thoroughly rinsed and dried at room temperature.

2.1.2 Chemicals and Instrumentation

Para nitro aniline, para chloro aniline, para bromo aniline, γ-acid [7-amino-1- naphthol -3- sulfonic acid](Fluka), resorcinol (Qualikems), 2, 4- dihydroxy benzophenone (Meark), 1-hydroxy benzotriazol (Aldrich), all other chemicals used in this study was of laboratory grade.

All melting points were determined on an electrothermal digital melting point apparatus and are uncorrected. IR spectra were recorded in KBr disks using a PYA UNICAM spectra 1000 FT-IR spectrophotometer. 1HNMR (400MHz) spectra were recorded on a VARIAN 400MHz spectrometer in DMSO as solvent and TMS as internal standard; chemical shifts are reported in d units (ppm). UV spectra were recorded on a Perkin Elmer Lamb 15 UV/Vis spectrophotometer.

2.2 Synthesis

2.2.1 Synthesis of Disazo Dyes (containing UV Absorber) 1-3 [19]

Para. Nitro aniline was diazotized by the following method:

p. nitro aniline (1.38gm, 0.01 mol) was dissolved in concentrated HCl (37% , 3ml) and poured over ice (50gm) at 0˚C, $NaNO_2$ (0.72 gm) was added dropwise over 30 min. the reaction mixture was stirred at 0˚C for 40 min and the excess nitrous acid was removed by adding a small amount of sulphamic acid. the resultant solution was added to γ-acid (2.4 gm, 0.01mol) which dissolve in the appropriate amount of aqueous sodium carbonate at 5-6˚C over 30–45 min. at PH 8–9. The coupling was stirred until PH was stabled {T1}[20].

Then the resultant mixture {T1} was filtrated and then diazotized in a similar manner as described above to obtain {T1A}.

2.2.1.1 Reaction of T1A with resorcinol (dye 1)

(T1A,0.01 mol) was treated with resorcinol (1.1gm, 0.01 mol) dissolved in 10% sodium hydroxide (10ml) and the mixture was stirred at PH 8.5 and 8-10˚C for 1h. The dye was salted out by addition of NaCl (15% w/v) at 80˚C.then filtrated and dried.

Dye 1: λ= 480nm, mp>300˚C yield 74%.

IR (KBr) υmax/cm^{-1}: 3426 (OH), 1494(N=N), 1212, 1107, 1050 (SO_3H).

^{1}HNMR (DMSO) ppm: δ 13.7, 12.45, 10 ppm (s, 3H, OH which are disappear in D_2O), 8.4–5.7ppm (m, 11H, aromatic H).

2.2.1.2 Reaction of T1A With 2, 4- dihydroxy benzophenone (dye 2)

(T1A,0.01 mol) was treated with 2, 4- dihydroxy benzophenone (2.14gm, 0.01mol) dissolved in 10% sodium hydroxide (16ml),the mixture was stirred at PH 8–9 and 8–10˚C for 1h. The dye was isolated by addition of NaCl (15% w/v) at 80˚C then filtrated and dried.

Dye 2: λ= 520 nm, mp>300˚C, yield 87%.

IR (KBr) υmax/cm^{-1}: 3448(OH), 1625(C=O), 1499(N=N), 1266, 1127, 1038(SO_3H).

^{1}HNMR (DMSO) ppm: δ13.9, 13.7, 12.4 ppm (s, 3H, OH which are disappear in D_2O), 8.3 – 5.5 ppm (m, 15H, aromatic H).

2.2.1.3 Preparation of Dye 3

2.2.1.3.1 Sulphonation of hydroxy benzotriazol[21]

In 1000 ml round –bottom flask, 20 gm of concentrated sulfuric acid was added, followed by addition of hydroxy benzotriazol (27gm) with frequent shaking. The mixture was warmed until a solid homogenous compound was formed (10min). Diphenyl ether (30ml) was added and the mixture was refluxed for 10h. Then cooled to room temperature and the excess of diphenyl ether were decanted.

2.2.1.3.2 Reaction of T1A with 1-hydroxy benzotriazol sulfonic acid (dye 3)

(T1A,0.01 mol) was treated with 1- hydroxy benzotriazol sulfonic acid (2.15gm, 0.01mol) dissolved in 10% sodium hydroxide (20ml) .The reaction mixture stirred at PH 8–9 and 8–10˚C until PH was stabled. The dye was salted out by addition of NaCl (15% w/v) at 80˚C then filtrated and dried.

Dye 3: λ=495nm, mp>300˚C, yield 85%.

IR (KBr) υmax/cm^{-1}:3430 (OH), 1487(N=N), 1191, 1103, 1042 (SO_3H).

^{1}HNMR (DMSO) ppm: δ 12.4, 10.91 ppm (s, 2H, OH which are disappear in D_2O), 8.39 - 6.8 ppm (m, 10H, aromatic H).

2.2.2 Synthesis of Disazo Dyes(containing UV Absorber)4-6 [19]

Para. cl Aniline was diazotized by the following method:
Para. cl aniline (1.275gm, 0.01 mol) was dissolved in concentrated HCl (37%, 3ml), poured over ice (50gm) at 0˚C. $NaNO_2$ (0.72 gm) was added dropwise over 30 min. the reaction mixture was stirred at 0˚C for 40 min and the excess nitrous acid was destroyed by adding a small amount of sulphamic acid.

The resultant solution was added to γ-acid (2.4 gm, 0.01mol) dissolved in the appropriate amount of aqueous sodium carbonate at 5–6˚C, over 30–45 min at PH 8–9. The coupling was stirred until PH was stabled {T2}[20]. Then the resultant mixture {T2} was filtrated and then diazotized in a similar manner as described above to obtain {T2A}.

2.2.2.1 Reaction of T2A with resorcinol (dye 4)

(T2A,0.01 mol) was treated with resorcinol (1.1gm, 0.01 mol) dissolved in 10% sodium hydroxide (10ml) and the mixture was stirred at PH 8.5 and 8–10˚C for 1h. The dye was isolated by addition of NaCl (15% w/v) at 80˚C then filtrated and dried.

Dye 4: λ= 520 nm, mp>300˚C, yield 78%.

IR (KBr) υmax/cm^{-1}: 3432 (OH), 1490 (N=N), 1285, 1181, 1051 (SO_3H).

^{1}HNMR (DMSO) ppm: δ 12.8, 12.5, 10.4 ppm (s, 3H, OH which are disappear in D_2O), 7.9 - 6.12ppm (m, 11 H, aromatic H).

2.2.2.2 Reaction of T2A With 2, 4- dihydroxy benzophenone (dye 5)

(T2A,0.01 mol) was treated with 2, 4- dihydroxy benzophenone (2.14gm, 0.01mol) dissolved in 10% sodium hydroxide (16ml),The mixture stirred at PH 8-9 and 8-10˚C for 1h. The dye was salted out by addition of NaCl (15% w/v) at 80˚C then filtrated and dried.

Dye 5: λ= 500nm, mp>300˚C, yield 83%.

IR (KBr) υmax/cm^{-1}: 34325(OH), 1656(C=O), 1509(N=N), 1205, 1097, 1041 (SO_3H).

^{1}HNMR (DMSO) ppm: δ 12.4, 12.3, 10.4 ppm (s, 3 H, OH which are disappear in D_2O), 7.98 - 6.23 ppm (m, 15 H, aromatic H).

2.2.2.3 Reaction of T2A with 1-hydroxy benzotriazol sulfonic acid (dye 6)

(T2A,0.01 mol) was treated with 1- hydroxy benzotriazol sulfonic acid (2.15gm, 0.01mol), prepared in a similar way mentioned above (2.2.1.3.1), dissolved in 10% sodium hydroxide (20ml) , the mixture stirred at PH 8-9 and 8-10˚C until PH was stabled. The dye was salted out by addition of NaCl (15% w/v) at 80˚C then filtrated and dried.

Dye 6: λ=515nm, mp>300˚C, yield 80%.

IR (KBr)υmax/cm^{-1}:3428(OH),1493(N=N), 1187, 1109,1035(SO_3H).

^{1}HNMR (DMSO) ppm: δ 12.4, 10.3ppm (s, 2H, OH which are disappear in D_2O), 7.84 – 5.6 pm (m, 10H, aromatic H).

2.2.3 Synthesis of Disazo Dyes(containing UV Absorber)7-9 [19]

Para. Br Aniline was diazotized by the following method

para. Br Aniline (1.72gm, 0.01mol) was dissolved in concentrated HCl (37% , 3ml) and poured over ice (50gm) at 0˚C. $NaNO_2$ (0.72 gm) was added dropwise over 30 min. the reaction mixture was stirred at 0˚C for 40 min. and the excess nitrous acid was removed by adding a small amount of sulphamic acid.

The resultant solution was added to γ - acid (2.4 gm, 0.01mol) which dissolved in the appropriate amount of aqueous sodium carbonate at 5-6˚C,

run over 30-45 min. at PH 8-9. The coupling was stirred until PH was stabled {T3}[20].

Then the resultant mixture {T3} was filtrated and then diazotized in a similar manner as described above to obtain {T3A}.

2.2.3.1 Reaction of T3A with resorcinol (dye 7)

(T3A, 0.01mol) was treated with resorcinol (1.1gm, 0.01mol) dissolved in 10% sodium hydroxide (10ml), the mixture was stirred at 8-10˚C, PH 8.5 for 1h. The dye was salted out by addition of NaCl (15% w/v) at 80˚C, then filtrated and dried.

Dye 7: λ= 530 nm, mp>300˚C, yield 79%.

IR (KBr) υmax/cm^{-1}: 3436 (OH), 1490(N=N), 1185, 1118, 1051 (SO_3H).

^{1}HNMR (DMSO) ppm: δ12.9, 12.4, 10.7 ppm (s, 3H, OH which are disappear in D_2O), 8.01 – 6.4 ppm (m, 11H, aromatic H).

2.2.3.2 Reaction of T3A with 2, 4- dihydroxy benzophenone (Dye 8)

(T3A,0.01 mol) was treated with 2, 4-dihydroxy benzophenone (2.14gm, 0.01mol) dissolved in 10% sodium hydroxide (16ml), The mixture stirred at PH 8–9, 8–10˚C for 1h. The dye was salted out by addition of NaCl (15% w/v) at 80˚C then filtrated and dried.

Dye 8: λ= 505 nm, mp > 300˚C, yield 81%.

IR (KBr) υmax/cm^{-1}:3408 (OH), 1656 (C=O), 1506(N=N), 1189, 1186, 1046 (SO_3H).

^{1}HNMR (DMSO) ppm: δ 13.9, 13.5, 11.7ppm (s, 3H, OH which are disappear in D_2O), 8.5–6.1ppm (m, 15H, aromatic H).

2.2.3.3 Reaction of T3A with 1- hydroxy benzotriazol sulfonic acid (Dye 9)

(T3A,0.01mol) was treated with 1-hydroxy benzotriazol sulfonic acid (2.15gm, 0.01mol), prepared in a similar way mentioned above (2.2.1.3.1), dissolved in 10% sodium hydroxide (20ml) , the mixture stirred at 8–10˚C, PH 8-9 until PH was stabled. The dye was salted out by addition of Nacl (15% w/v) at 80˚C then filtrated and dried.

Dye 9: λ= 520 nm, mp>300˚C, yield 79%.

IR (KBr) υmax/cm^{-1}: 3429 (OH), 1489(N=N), 1185, 1135, 1053(SO_3H).

^{1}HNMR (DMSO) ppm: δ 11.7, 10 ppm (s, 2H, OH which are disappear in D_2O), 7.8 - 6.8 ppm (m, 10 H, aromatic H).

3. Dyeing Procedures, Color Measurements and Fastness Testing of the Dyed Samples

3.1 Dyeing of Wool Fabric[22]

All dyeing were carried out in distilled water. All the synthesized dyes (1-9) and intermediate (traditional dyed) (T1 – T3), were applied at a range of dye conc. 0.5–3% (o.w.f). The dyeing bath was adjusted at pH 3-8 by buffer solutions with a 1:100 liquor ratio (10% Na_2SO_4 concentration). Each dyeing was performed at 60˚C, allowing the temperature of the dye bath raised to 70–100˚C over 30 min and the dyeing continued at these temperature for different time intervals (30–150min). At the end of the dyeing process, the samples were thoroughly rinsed and air-dried.

3.2 Color Measurements

3.2.1 Color Strength

The colorimetric analysis of the dyed samples was performed using a Hunter Lab ultra Scan® PRO spectrophotometer.

The corresponding colour strength value (K/S) was assessed by applying the Kubelka Munk equation as follows[23].

$$K/S = (1-R)^2 / 2R - (1-R_o)^2 / 2R_o$$

where:

R = Decimal fraction of the reflectance of the dyed fabric

R_o = Decimal fraction of the reflectance of the undyed fabric

K = Absorption coefficient.

S = Scattering coefficient

3.2.2 Fastness Testing

The dyed washed samples were tested by standard ISO methods. The specific testes were ISO 105-X12(1987), ISO 105-co4 (1989), ISO105-EO4 (1989), ISO 105-BO2 (1988) corresponding to color fastness to rubbing, washing, perspiration and light, respectively.

3.2.3 Irradiation

Samples 10x10 cm of dyed fabrics mounted on a white chart paper and irradiated using a XENOTEST 1200 apparatus at a relative air humidity of 65% and 50˚C with duration from 0 to 175 hours.

3.2.4 The Total Color Difference (ΔE)

3.2.4.1 CIE Lab Difference

Now, in a lot of dye houses, there is a datamatch system which helps colorist to obtain different shades and to judge about the acceptance of these shades against a particular standard. The most widely used equation is CIE lab difference equation.

$$\Delta E = L^2 + [(a^2 + b^2)]^{1/2}$$

ΔE: the total difference between the sample and the stander

a: represents the red – green axis

b: the yellow – blue axis

L: describes lightness

4. Results and discussion

4.1 Dyes Structure

The chemical structure of intermediate azo dyes (traditional dyes) (T1, T2, and T3) and synthesized anti-uv azo dyes (1–9) are given in Figures 1 and 2.

4.2 Elucidation of Synthesized Dyes Structures

4.2.1 IR Analysis

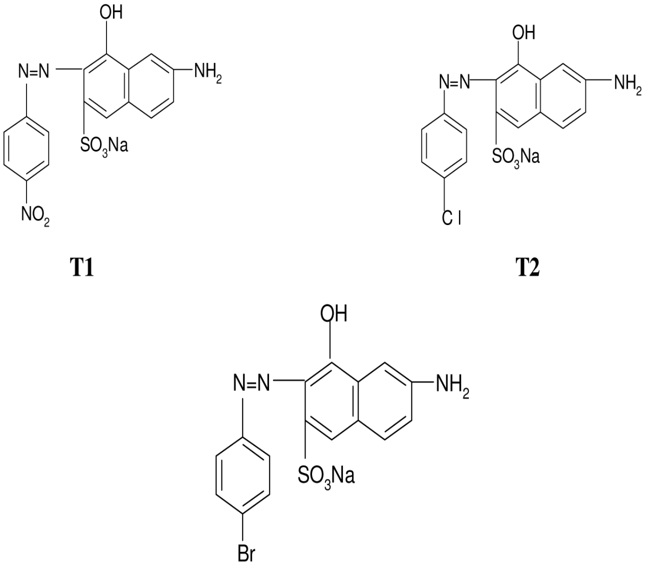
The IR spectra of the synthesized dyes based on γ-acid (1–9) showed a characteristic absorption band of (–OH) group appear at the range (3448 ~ 3426 cm^{-1}), also, showed absorption band at the range (105 ~ 14871cm^{-1}) corresponding to azo group (N=N).

Three characteristic bands appeared at 1285, 1181, 1051 (e.g. dye 1) which indicate the presence of –SO$_3$ group.

The IR spectral data also revolved absorption band at (1625~1658 cm^{-1}) for carbonyl group (C=O) of dyes 2, 5 and 8.

4.2.2 1H-NMR Analysis

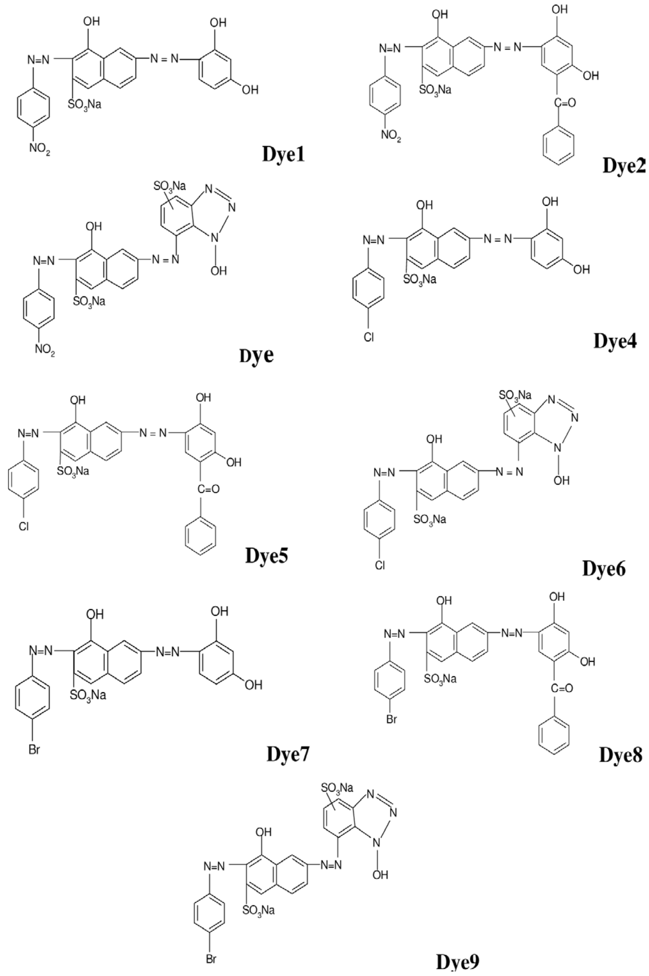
^{1}HNMR spectra of synthesized dyes based on γ-acid (1–9), in all these ^{1}HNMR spectra, the must characteristic signals are: d ppm at (13.9–10) corresponding to (OH) protons groups which are disappear in D2O; d ppm at (8.4 – 5.7) are assigned to the aromatic protons.


T1

T2

T3

Figure 1. Intermediate azo dyes (traditional dyes).


Dye1

Dye2

Dye

Dye4

Dye5

Dye6

Dye7

Dye8

Dye9

Figure 2. Anti-uv azo dyes.

4.3 Dyeing Performance and Fastness Properties of the Synthesized Anti-UV Azo Dyes

4.3.1 Factors Affecting Dyeing of Wool Fabrics

4.3.1.1 Effect of dyeing pH

Wool fabrics (0.5g) were dyed with 2% (w.o.f) intermediate azo dyes (T4–T6) and anti- UV azo dyes (1-9) at pH (3-8) and L.R 1:50. Dyeing was continued for 60 mins at 95˚C. After that, the dyed samples were rinsed, washed and air dried. The color strength (K/S) values of dyed washed samples were cited in Table 1.

From Table 1 it can be observed that the higher color strength values for wool samples dyed with T3, Dye3, 4, 6, 7, 9 were obtained at pH 3 while T1,T2, dye2, 5, 8, gives highest color strength values at pH 4 and dye 1 gives higher color strength values at pH 5.

Table 1. Effect of dyeing pH on the colour strength (K/S) values of wool fabric dyed with dye intermediates (T1-T3) and anti-uv azo dyes (1-9) (2% (w.o.f.), L.R 1:50, for 60 min)

Dye No.	K / S					
	pH 3	pH 4	pH 5	pH 6	pH 7	pH 8
T1	4.44	8.53	6.37	5.13	4.08	2.42
T2	6.99	7.44	5.59	4.31	2.8	2.73
T3	11.21	10.69	4.57	1.33	1.62	1.34
Dye1	2.9	4.41	4.79	4.21	1.83	0.99
Dye2	9.57	12.57	9.38	3.87	3.24	2.82
Dye3	8.51	7.27	4.72	4.39	4.1	3.11
Dye4	7.66	6.53	4.91	4.87	3.11	3.14
Dye5	7.32	7.78	7.04	4.84	4.55	3.11
Dye6	4.87	4.04	3.65	2.13	1.94	1.86
Dye7	6.61	6.29	5.24	3.81	4.61	2.31
Dye8	2.81	4.68	4.8	3.89	2.95	2.77
Dye9	4.99	3.72	3.52	2.09	2.02	1.92

4.3.1.2 Effect of dyeing temperature

wool fabrics were dyed with intermediate azo dyes (T1, T2, T3) and anti- UV azo dyes (1-9) and temperature (60-100˚C) at the suitable pH as mentioned before. Data of color strength (K/S) for dyed washed samples were listed in Table 2.

From Table 2 it can be seen that increasing temperature from 60 to 80˚C leads to a slight increase in color yield values (K/S). Increasing temperature more than 80˚C leads to an improvement in color yield values. The maximum dyeability and color strength were obtained at 100˚C this holds true for all dyes used.

4.3.1.3 Effect of dyeing time

Wool fabrics were dyed with intermediate azo dyes (T1, T2, T3) and anti- UV azo dyes (1–9) at the suitable pH and time (30 – 150 min). The color strength for the dyed washed samples was tabulated in Table 3.

Table 3 shows that an increase in dyeing time from 30 min to 60 min increased K/S for all dyes. After 60 min dyeing, the colour strength values nearly levels off or a very slight improvement takes place.

4.3.1.4 Effect of dye concentrations

Wool fabrics were dyed with intermediate azo dyes (T1, T2, and T3) and anti- UV azo dyes (1–9), (0.5%–3% w.o.f.) at the suitable pH. The color strength (K/S) were measured and cited in Table 4.

Table 2. Effect of dyeing temperature on the colour strength (K/S) values of wool fabric dyed with dye intermediates (T1–T3) and anti-uv azo dyes (1–9) (2% (w.o.f.), L.R 1:50, for 60 min)

Dye No.	K / S				
	60˚C	70˚C	80˚C	90˚C	100˚C
T1	5.49	6.29	6.81	6.95	7.51
T2	3.57	3.76	3.85	5.35	5.49
T3	5.47	6.68	7.37	7.68	8.19
Dye1	2.76	3.07	3.99	4.39	5.05
Dye2	4.9	6.04	7.37	7.39	8.08
Dye3	4.81	5.04	6.07	6.12	6.96
Dye4	2.61	3.93	4.83	5.36	6.37
Dye5	2.02	2.81	3.82	6.85	8.36
Dye6	1.46	1.78	2	2.88	3.23
Dye7	3.04	3.35	4.43	4.59	5.11
Dye8	3.47	4.03	6.11	10.53	11.18
Dye9	1.73	1.78	2.41	2.64	2.84

Table 3. Effect of dyeing time on the colour strength (K/S) values of wool fabric dyed with dye intermediates (T1–T3) and anti-uv azo dyes (1–9) (2% (w. o. f.), L. R 1:50, dyeing temperature: 100˚C)

Dye No.	K / S				
	30 min.	60 min.	90 min.	120 min.	150 min.
T1	5.19	7.01	7.14	7.27	7.79
T2	5.51	5.85	5.92	6.05	7.49
T2	7.05	7.28	8.31	8.77	8.86
Dye1	3.54	3.71	4.23	4.45	4.79
Dye2	8.37	8.93	9.34	10.45	10.74
Dye3	5	5.4	6.26	6.45	7.78
Dye4	3.93	4.97	4.99	5.25	5.82
Dye5	7.21	8.09	8.72	10.57	11.72
Dye6	3.18	3.5	3.64	4.51	5.25
Dye7	2.33	2.54	3.37	3.8	3.87
Dye8	8.02	8.05	8.15	8.6	9.01
Dye9	3.28	3.45	4.18	4.23	5.67

Table 4 shows that as the dye concentration increases from 0.5 % to 3%, the color strength also increases for all dyes.

4.3.1.5 Fastness properties

Fastness properties of intermediate dyes and anti-uv dyes (T1–T3, Dye1-Dye9) are shown in Table 5. Results show that very good fastness properties for both intermediate dyes and anti uv dyes; as for washing and perspiration fastness properties, the anti uv dyes show better fastness compared with intermediate dyes ranging from good to very good.

Light fastness also improved for anti-uv dyes against intermediate dyes showing very good light fastness.

Table 4. Effect of dye concentration on the color strength (K/S) values of wool fabric dyed with dye intermediates (T1–T3) and anti-uv azo dyes (1–9) (L.R 1:50, dyeing temp 100˚C for 60 min)

Dye No.	K /S					
	0.5%	1%	1.5%	2%	2.5%	3%
T1	3.25	4.65	12.24	13.69	17.6	18.8
T2	5.56	7.54	12.45	13.91	14.07	17.18
T3	3.13	9.78	15.02	19.2	19.73	21.74
Dye1	3.3	4.89	5.31	6.2	9.09	12.11
Dye2	4.88	8.2	15.43	20.69	21.2	21.33
Dye3	3.81	6.93	12.66	16.53	17.61	20.87
Dye4	3.6	5.91	11.81	13.33	14.27	15.49
Dye5	3.56	7.99	9.09	10.38	12.86	15.83
Dye6	1.77	3.51	6.08	6.36	7.22	7.58
Dye7	3.58	8.37	9.77	12.73	16.2	16.86
Dye8	2.31	5.07	6.36	6.92	7.53	8.48
Dye9	1.79	3.35	4.54	5.52	6.87	8.15

4.3.1.6 *The total color difference (ΔE)*

Table 6 reveals that with increasing the time of irradiation of dyed wool samples, the rate of fading increases for all dye intermediates T1, T2 and T3. Following the order T3 >T1 > T2. This can be attributed to the electro negativity of NO2 > Cl >Br groups.

The rate of fading for nylon samples dyed with Dye1-Dye9 is less than that for samples dyed with T1-T3. This can be explained by the presence of anti ultraviolet functional finishing group in dyes structure.

For dyed samples with Dye1-Dye3 it can be observed that the light fading of samples dyed with Dye3 is less than that with Dye2 and Dye1 following the order Dye1 > Dye2> Dye 3. This can be attributed to the greater reactivity of triazol present in 1- hydroxy benzotriazol sulfonic acid anti UV in Dye3, Dye6 and Dye 9, also, due to the present of carbonyl group in 2,4-dihydroxy benzophenone in Dye2,Dye5 and Dye8.

5. Conclusion

Novel nine azo dyes containing anti-uv absorbers (anti-uv dyes) were prepared using primary aromatic amines (P.No$_2$, Cl, Br aniline) and γ – acid coupler. Resorcinol, 2, 4- dihydroxy bezophenone and 1- hydroxyl benzotriazol

Table 5. Fastness Properties of wool samples dyed with dye intermediates (T1–T3) and anti-uv azo dyes (1–9) (2% dye, L.R 1:50, and dyeing for 60 min. at 100˚C)

Dyes	Crocking fastness		Washing fastness			Acidic perspiration			Alkaline perspiration			Light fastness
	Dry	Wet	St.*	St.**	Alt.	St.*	St.**	Alt.	St.*	St.**	Alt.	
T1	4 -5	4 -5	3-4	3 -4	3	3 - 4	3 -4	3	3 -4	3 -4	3	5
Dye1	4 -5	4 -5	4	4	4	4	4	3	4	4	4	6
Dye2	4 -5	4 - 5	4	4	4	4	4	4	4	4	4	6-7
Dye3	4 -5	4 -5	4	4	4	4	4	4	4	4	4	6-7
T2	4 -5	4 -5	3-4	3-4	3	3 -4	3 -4	3	3 -4	3 -4	3	5
Dye4	4 -5	4 -5	4	4	4	4	4	4	4	4	4	6
Dye5	4 -5	4 -5	4	4	4	4	4	4	4	4	4	6-7
Dye6	4 -5	4 -5	4	4	4	4	4	4	4	4	4	6-7
T3	4 -5	4 -5	3 - 4	3 -4	3	3-4	3-4	3	3-4	3-4	3	5
Dye7	4 -5	4 -5	4	4	4	4	4	4	4	4	4	6
Dye8	4 -5	4 -5	4	4	4	4	4	4	4	4	4	6-7
Dye9	4 -5	4 -5	4	4	4	4	4	4	4	4	4	6-7

St.* = Staining on cotton
St. **= Staining on wool
Alt. = Alteration in color

Table 6. The rate of fading of wool fabric dyed with dye intermediates (T1–T3) and anti-uv azo dyes (1–9) (2% dye, L.R 1:50, dyeing for 60 min. at 100˚C and suitable pH for each dye)

Time of Irradiation In hrs		T1	Dye1	Dye2	Dye3	T2	Dye 4	Dye5	Dye 6	T3	Dye7	Dye8	Dye9
0h	L	51. 16	42. 33	25. 43	26. 69	32. 65	32. 56	32. 25	30. 53	50. 02	30. 22	28. 67	27. 43
	a	19. 81	16. 17	34. 28	28. 74	31. 26	22. 10	18. 18	19. 98	33. 39	36. 10	36. 64	28. 63
	b	4. 64	9. 96	15. 24	13. 27	11. 23	18. 44	- 15. 04	29. 21	7. 65	22. 20	16. 43	14. 45
	ΔE	55. 06	46. 40	45. 32	41. 41	46. 65	43. 46	38. 36	37. 63	60. 63	52. 05	49. 34	42. 20
35h	L	58. 45	50. 55	25. 14	27. 50	47. 00	35. 06	27. 37	30. 73	55. 78	30. 12	29. 19	27. 70
	a	14. 43	12.00	34. 65	28. 46	17. 00	22. 33	25. 94	22. 27	24. 32	36. 26	37. 06	28. 64
	b	5. 08	10. 06	15. 54	13. 15	13. 65	18. 20	15. 18	14. 12	5. 96	22. 29	16. 74	14. 70
	ΔE	60. 42	52. 92	45. 54	41. 70	51. 81	45. 38	40. 65	40. 49	61. 14	52. 14	50. 06	42. 47
70h	L	63. 54	61. 31	25. 81	27. 30	51. 12	35. 32	27. 85	31. 28	59. 89	31. 33	29. 12	28. 85
	a	9. 94	5.84	34. 94	28. 61	15. 03	22. 22	27. 07	21. 81	14. 35	35. 58	37. 21	27. 62
	b	4. 63	6. 91	15. 39	13. 32	12. 62	18. 36	15. 19	13. 80	6. 63	22. 60	16. 80	14. 63
	ΔE	64. 48	61. 97	46. 08	41. 73	54. 76	45. 59	41. 71	40. 55	62. 03	52. 52	50. 15	42. 53
105h	L	66. 66	61. 10	26.76	27. 63	50. 37	36. 53	28. 10	30. 88	61. 99	30. 99	29. 29	28. 35
	a	7. 06	8. 77	35. 60	29. 15	21. 01	23. 39	27. 12	22.40	12. 07	36. 30	37. 06	28. 54
	b	3. 89	9. 07	16. 27	13. 40	10. 76	17. 30	15. 71	14.19	6. 56	23. 25	16. 95	14. 71
	ΔE	67 15	62. 39	47. 41	42. 34	55.62	46. 70	42. 09	40. 70	63. 50	53. 09	50. 19	42. 83
140h	L	70. 03	62.12	27. 06	29. 01	57. 20	36. 77	28. 47	30. 78	64. 53	32. 70	29. 67	28.38
	a	12. 97	5. 40	36. 23	28. 53	14. 81	23.53	27. 28	22. 44	10. 32	37. 41	37. 75	28. 77
	b	7. 63	6. 44	16. 50	14. 10	9.14	17. 60	16. 18	14. 39	5. 82	24. 40	17. 34	15. 00
	ΔE	71. 63	62. 69	48. 13	43. 06	59. 79	47. 07	42. 62	40. 72	65.61	55. 35	51. 05	43. 11
175h	L	71. 35	61. 55	29. 30	28. 54	60. 47	36. 66	28. 44	31. 84	65. 14	33. 96	29. 62	28. 34
	a	13. 31	9. 31	39. 45	29. 69	8. 42	23. 83	27. 63	22.44	10. 72	37. 95	38. 12	29. 25
	b	7. 64	9. 25	18. 36	13.75	9. 34	17. 93	16. 78	14. 17	5. 78	25. 79	17. 11	15. 12
	ΔE	72. 99	62. 93	52. 46	43. 07	61. 76	47. 26	43. 06	41. 45	66. 27	57. 08	51. 22	43.44

sulfonic acid were used as UV absorbers. Polyfunctional dyes Dye3, Dye6, Dye9 containing 1- hydroxyl benzotriazol sulfonic acid anti UV absorber gives less fading than other dyes, due to the presence of triazol group. Followed by Dye2, Dye5, Dye8 which have 2, 4- dihydroxy bezophenone as a UV absorber. Dye1, Dye4, Dye7 containing resorcinol as UV absorber gives highest fading results.

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