

Synthesis and Application of Functional (Anti-UV) Azo - dyes on Nylon Fabrics: Part I

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NINE novel azo dyes containing UV absorber (anti-UV dyes) were synthesized by diazotization of primary aromatic amines (p.NO₂, p.Cl, p.Br aniline) and then coupling with J- acid coupler. The resultant intermediates were also diazotized and coupled with anti-UV functional finishing groups (resorcinol, 2, 4- dihydroxy benzophenone, 1- hydroxy benzotriazol sulfonic acid UV absorbers). The structure of the synthesized dyes was fully elucidated using FTIR and ¹H-NMR. All synthesized dyes were applied on nylon fabrics. Fabrics dyed with anti-UV dyes were tested for color strength (K/S), rate of fading (ΔE) values and fastness properties.

Keywords: Synthesis, Characterization, Azo dyes, Dyeing, Color strength (K/S), UV absorbers and Nylon fabric.

As known, UV radiation emitted by the sun in the range between 100 and 400 nm is subdivided into UV-C (100-280nm), UV-B (280- 315nm) and UV- A (315-400nm)⁽¹⁻⁴⁾.

As for UV radiation type C which is dangerous to living species, higher layers of the atmosphere absorb this type of radiation. Human skin has to be protected against excessive radiation of the UV-B type which is proved to be dangerous in its excessive range. It was proved that excessive radiation of this range is the origin of premature skin ageing, sunburns, allergies and even skin cancer. The UV-A (λ =315-400nm) radiation is less dangerous but also its over dose can result in similar effects as described above⁽⁵⁾.

Recently, UV radiation (280–400 nm) has received growing attention from researchers because of the increased levels of UV radiation reaching the earth's surface, due to stratospheric ozone depletion⁽⁵⁾.

Accordingly, the awareness of the need for protection against harmful UV radiation rapidly increases attention for textiles designed for protective clothing, including the protection against ultraviolet radiation (UV), which ranges from 100 to 400 nm.^(1, 3, 4, 6-9)

Fabric color also has a fundamental importance in UV protection; dyed fabrics protect more than undyed ones and their protection levels rise with the increase in dye concentration⁽¹⁰⁾. In general, light colors reflect solar radiation more efficiently than dark ones^(11, 12), allowing incident radiation to penetrate through the fabric with reflecting actions (scattering).

High light fastness of dyed materials is important especially for garment, automobile colored upholstery, which can be exposed to direct sunlight and temperature above 50°C.

The present study is an attempt to synthesis a novel anti-UV azo dyes by incorporating an ultraviolet absorber (UVA) into a dye chromophore to obtain functional anti-UV dyes.

UV absorbers are organic or inorganic compounds which have been utilized to protect polymeric materials from photo degradation caused by sunlight or ultra-violet rich artificial light. UV absorbers are often used to protect material properties of polymers or textiles, *e.g.* improvement of the light fastness of textile coloration⁽⁷⁾.

Experimental

Materials

Substrate

Scoured nylon fabrics (172 g/m²) were supplied from Misr for Spinning and Weaving Company, Mahalla El- Kobra., Egypt. Nylon fabric was further treated with a solution containing 2g/L nonionic detergent (Hostapal ® CV-Clariant), at 60°C for 30 min, then the fabrics were thoroughly rinsed with water and air dried at room temperature.

Chemicals and instrumentation

Para nitro aniline, para chloro aniline, para bromo aniline, J- acid[6-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 were of laboratory reagent 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 δ units (ppm). UV spectra were recorded on a Perkin Elmer Lamb 15 UV/Vis spectrophotometer.

Synthesis

Synthesis of disazo dyes (containing UV absorber) 1-3⁽¹³⁾

P.Cl Aniline was diazotized by the following method: P.Cl Aniline (1.275gm, 0.01 mol) was dissolved in concentrated HCl (37%, 3ml), poured over ice
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(50gm) at 0°C. NaNO₂ (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 J- 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 {T1} ⁽¹⁴⁾. Then the resultant mixture {T1} was filtrated and then diazotized in a similar manner as described above {T1A}.

Reaction of T2A 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 1hr. The dye was isolated by addition of NaCl (15% w/v) at 80 °C then filtrated and dried.

Dye 1: λ= 495nm, mp>300 °C, yield 75%.

C₂₂H₁₄N₄O₆SCLNa (520), [M⁺]=520.

IR (KBr) ν_{max}/cm⁻¹: 3419 (OH), 1474(N=N), 1275, 1187, 1048 (SO₃H).

¹HNMR (DMSO) ppm: δ 12.6, 12.2, 10.1 ppm (s, 3H, OH disappear in D₂O), 8.1 – 5.7 ppm (m, 11 H, aromatic H).

Reaction of T2A 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 stirred at pH 8-9 and 8-10 °C for 1hr. The dye was salted out by addition of NaCl (15% w/v) at 80 °C then filtrated and dried.

Dye 2: λ= 500nm, mp>300 °C, yield 87%.

IR (KBr) ν_{max}/cm⁻¹: 3428(OH), 1619(C=O), 1493(N=N), 1270, 1219, 1053 (SO₃H).

¹HNMR (DMSO) ppm: δ 12.6, 12.2, 10 ppm (s, 3 H, OH disappear in D₂O), 7.8 - 6ppm (m, 15 H, aromatic H).

Preparation of dye 3

1. *Sulphonation of hydroxy benzotriazol* ⁽¹⁵⁾: 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 10hr, then cooled to room temperature and the excess of diphenyl ether was decanted.

2. *Reaction of T1A with 1-hydroxy benzotriazol sulfonic acid (dye3):* (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 was 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=505nm, mp>300 °C, yield 81%.

IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3446(OH), 1495(N=N), 1269, 1229, 1053(SO₃H).

¹HNMR (DMSO) ppm: δ 12, 10 ppm (s, 2H, OH disappear in D₂O), 7.9-6 ppm (m, 10H, aromatic H).

Synthesis of disazo dyes (containing UV absorber) 4-6 ⁽¹³⁾

P. nitro aniline was diazotized by the following method: p. nitro aniline (1.38 gm, 0.01 mol) was dissolved in concentrated HCl (37% , 3ml) and poured over ice (50 gm) at 0 °C, NaNO₂ (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 J- acid (2.4 gm, 0.01 mol) 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 {T2} ⁽¹⁴⁾ .

Then, the resultant mixture {T2} was filtrated and diazotized in a similar manner as described above {T2A}.

Reaction of T1A with resorcinol (dye 4): (T2A, 0.01 mol) was treated with resorcinol (1.1 gm, 0.01 mol) dissolved in 10% sodium hydroxide (10 ml) and the mixture was stirred at pH 8.5 and 8-10 °C for 1 hr. The dye was salted out by addition of NaCl (15% w/v) at 80 °C. then filtrated and dried.

Dye 4: $\lambda = 495 \text{ nm}$, mp > 300 °C yield 70%.

IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3446 (OH), 1485(N=N), 1271, 1217, 1051 (SO₃H).

¹HNMR (DMSO) ppm: δ 13.7, 12.3, 10.3 ppm (s, 3H, OH disappear in D₂O), 8.4-6.1 ppm (m, 11H, aromatic H).

Reaction of T2A with 2, 4- dihydroxy benzophenone (dye 5): (T2A, 0.01 mol) was treated with 2, 4- dihydroxy benzophenone (2.14 gm, 0.01 mol) dissolved in 10% sodium hydroxide (16 ml), the mixture was stirred at pH 8-9 and 8-10 °C for 1 hr. The dye was isolated by addition of NaCl (15% w/v) at 80 °C then filtrated and dried.

Dye 5: $\lambda = 505 \text{ nm}$, mp > 300 °C, yield 82%.

IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3441(OH), 1623(C=O), 1483(N=N), 1275, 1112, 1054(SO₃H).

¹HNMR (DMSO) ppm: δ 14, 13.7, 11.7 ppm (s, 3H, OH disappear in D₂O), 8.2 - 6.2 ppm (m, 15H, aromatic H).

Reaction of T2A with 1-hydroxy benzotriazol sulfonic acid (dye 6): (T2A, 0.01 mol) was treated with 1- hydroxy benzotriazol sulfonic acid (2.15 gm, 0.01 mol), prepared in a similar way mentioned above, dissolved in 10% sodium hydroxide (20 ml) , the mixture was 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: $\lambda = 495 \text{ nm}$, mp > 300 °C, yield 83%.

IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3445 (OH), 1496(N=N), 1213, 1106, 1048 (SO₃H).

¹HNMR (DMSO) ppm: δ 11.2, 10.2 ppm (s, 2H, OH disappear in D₂O), 8.4 - 6.3 ppm (m, 10H, aromatic H).

Synthesis of disazo dyes(containing UV absorber)7-9⁽¹³⁾

p. Br Aniline was diazotized by the following method: p. Br Aniline (1.72gm, 0.01 mol) was dissolved in concentrated HCl (37% , 3ml) and poured over ice (50gm) at 0 °C. NaNO₂ (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 J- 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} ⁽¹⁴⁾.

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

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, H8.5 for 1hr. The dye was salted out by addition of NaCl (15% w/v) at 80 °C, then filtrated and dried.

Dye 7: $\lambda = 495\text{nm}$, mp>300 °C, yield 73%.

IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3431 (OH), 1492(N=N), 1264, 1191, 1049 (SO₃H).

¹HNMR (DMSO) ppm: δ 13.2, 12.6, 10.5 ppm (s, 3H, OH disappear in D₂O), 8.1 – 5.7 ppm (m, 11H, aromatic H).

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 was stirred at pH 8-9, 8-10 °C for 1hr. The dye was salted out by addition of NaCl (15% w/v) at 80 °C then filtrated and dried.

Dye 8: $\lambda = 495\text{nm}$, mp>300 °C, yield 85%.

IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3443 (OH), 1623 (C=O), 1494(N=N), 1272, 1123, 1055 (SO₃H).

¹HNMR (DMSO) ppm: δ 12.5, 12.4, 10.1ppm (s, 3H, OH disappear in D₂O), 7.8-6.08ppm (m, 15H, aromatic H).

Reaction of T3A with 1- hydroxy benzotriazol sulfonic acid (Dye 9): (T3A,0.01 mol) was treated with 1- hydroxy benzotriazol sulfonic acid (2.15gm, 0.01mol), prepared in a similar way mentioned above, dissolved in 10% sodium hydroxide (20ml), the mixture was 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: $\lambda = 495\text{nm}$, mp>300 °C, yield 82%.

IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3454 (OH), 1495(N=N), 1265, 1191, 1049(SO₃H).

¹HNMR (DMSO) ppm: δ 11.6, 10.1 ppm (s, 2H, OH disappear in D₂O), 7.8 - 6.3 ppm (m, 10 H, aromatic H).

*Dyeing procedures, color measurements and fastness testing of the dyed samples**Dyeing of nylon fabric*

All dyeings were carried out in distilled water. The dyeing of nylon fabrics follows a traditional exhaustion dyeing procedure⁽¹⁶⁾. The dye baths were prepared with the (T1- T3) and synthesized dyes (1-9) at a range of dye conc. (0.5-3% o.w.f). The pH of the dyeing bath was adjusted at 3, 4, 5, 6,7 and 8 by buffer solutions (acetic acid and/or sodium carbonate). The liquer ratio was kept at 1:50. The nylon fabrics were immersed into the dyeing bath at initial dyeing temperatures 40 °C for 10 min, then the temperature raised to 60,70,80,90 and 100 °C and the dyeing continued at these temp. for different time intervals (30-150 min). After dyeing, all the dyed samples were washed with (3gm/L) of non ionic detergent solution at 50 °C for 30 min⁽¹⁷⁾ and air dried.

Color measurements

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⁽¹⁸⁾.

$$K/S = (1-R)^2 / 2R - (1-R_0)^2 / 2R_0$$

where:

R = Decimal fraction of the reflectance of the dyed fabric.

R₀ = Decimal fraction of the reflectance of the undyed fabric.

K = Absorption coefficient.

S = Scattering coefficient.

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.

Irradiation: Samples 10x10 cm of dyed fabrics were 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 35 to 175 hr.

The total color difference (ΔE)

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⁽¹⁶⁾.

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

ΔE: the total difference between the sample and the stander.

a: represents the red – green axis.

b: the yellow – blue axis.

L: describes lightness.

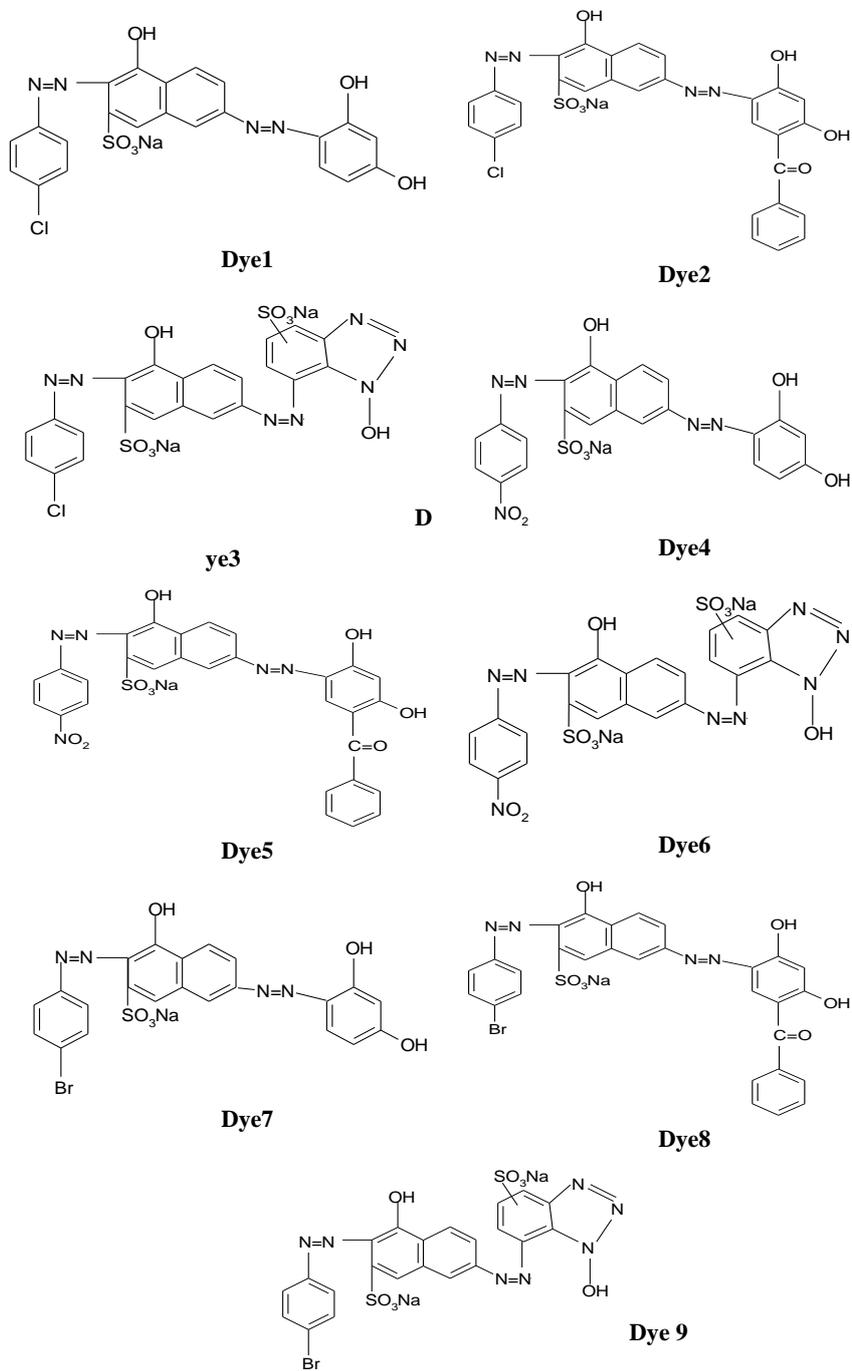


Fig. 2. Anti-UV azo dyes.

*Dyeing performance and fastness properties of the synthesized anti-UV azo dyes**Factors affecting dyeing of nylon fabrics*

Effect of dyeing pH: Nylon fabrics (0.5g) were dyed with 2% w.o.f intermediate azo dyes (T1, T2, T3) and anti-UV azo dyes (1-9) at pH (3-8) and L.R 1:50. Dyeing was continued for 60 min 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 T1, T2, Dye6, Dye9 were obtained at pH 3 while T3, Dye3, Dye4 give the highest color strength (K/S) values at pH 4 and dyes Dye1, Dye2, Dye5, Dye7, Dye8 give higher color strength (K/S) at pH 5.

TABLE 1. Effect of dyeing pH on the colour strength (K/S) values of nylon 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).

PH	Color strength (K/S)											
	T1	T2	T3	Dye1	Dye2	Dye3	Dye4	Dye5	Dye6	Dye7	Dye8	Dye9
3	27.84	25.93	21.1	25	21.51	19.18	23.02	11.54	22.17	23.25	21.1	22.17
4	26.37	25.71	22.5	25.89	22.29	20.79	23.62	17.4	20.9	24.24	21.53	19.59
5	26.14	24.03	21.69	27.01	25.28	19.79	21.23	22.02	18.9	26.89	23.16	17.57
6	25.22	23.43	19.39	26.65	22.63	18.08	19.19	10.18	15.01	23.8	21.84	17.21
7	21.41	22.58	19.13	23.6	21.49	17.61	19.74	8.78	11.67	21.92	18.54	14.26
8	19.23	16.73	13.12	21.77	20.46	12.43	12.93	5.93	6.19	20.93	17.4	13.99

Effect of dyeing temperature: Nylon fabrics (0.5g) were dyed with 2% w.o.f intermediate azo dyes (T1, T2, T3) and anti-UV azo dyes (1-9) at the suitable pH and L.R 1:50. Dyeing was continued for 60 min and temperature varied from (60-100°C). After that, the dyed samples were rinsed, washed and air dried. 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.

TABLE 2. Effect of dyeing temperature on the colour strength (K/S) values of nylon 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).

Temp.	Color strength (K/S)											
	T1	T2	T3	Dye1	Dye2	Dye3	Dye4	Dye5	Dye6	Dye7	Dye8	Dye9
60	24.08	21.36	20.93	21.05	12.39	16.3	22.42	18.79	20.82	21.8	11.7	20.33
70	25.95	22.56	21.69	21.63	13.13	16.43	23.1	18.87	20.96	24.24	12.9	21.27
80	26	22.7	22.53	22.02	13.72	18.03	24.16	19.12	21.19	25.05	14.45	21.77
90	26.45	24.47	22.59	22.78	14.51	20.17	24.21	19.36	21.59	25.13	15.25	22.29
100	27.07	25.4	22.69	22.91	15.33	20.62	24.37	20.02	21.68	25.5	19.78	23.48

Effect of dyeing time: Nylon fabrics (0.5g) were dyed with 2% w.o.f. intermediate azo dyes (T1, T2, T3) and anti-UV azo dyes (1-9) at the suitable pH and L.R 1:50, at 100°C and time was varied from (30-150 min). After that, the dyed samples were rinsed, washed and air dried. The color strength for the dyed washed samples were tabulated in Table 3.

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

TABLE 3. Effect of dyeing time on the colour strength (K/S) values of nylon 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).

Time	Color strength (K/S)											
	T1	T2	T3	Dye1	Dye2	Dye3	Dye4	Dye5	Dye6	Dye7	Dye8	Dye9
30	23.05	24.25	20.39	19.3	13.24	17.15	22.24	18.06	19.05	21.48	19.88	11.55
60	23.86	24.78	21.05	20.39	13.84	20.06	22.42	18.46	19.78	21.85	22.79	19.81
90	24.34	24.87	21.36	21.68	14.87	20.41	22.87	18.61	20.13	22.18	23.08	20.84
120	24.41	25.55	23.74	23.76	16.15	21.01	22.95	18.79	20.64	24.21	23.4	20.9
150	24.78	27.53	23.84	25.9	23.16	26.00	25.24	19.02	21.27	25.07	25.64	24.16

Effect of dye concentrations: Nylon fabrics (0.5g) were dyed with intermediate azo dyes (T1, T2, T3) and anti-UV azo dyes (1-9), (0.5%-3% w.o.f.) at the suitable pH and L.R 1:50, at 100°C for 60 min, then, the dyed samples were rinsed, washed and air dried. The color strength (K/S) were measured and cited in Table 4.

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

TABLE 4. Effect of dye concentration on the color strength (K/S) values of nylon 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).

Conc. %	Color strength (K/S)											
	T1	T2	T3	Dye1	Dye2	Dye3	Dye4	Dye5	Dye6	Dye7	Dye8	Dye9
0.5	18.71	12.13	4.83	17.95	6.47	6.21	13.84	5.36	5.04	10.55	5.44	3.7
1	25.26	23.41	13.56	23.23	11.46	14.25	18.3	5.93	12.33	20.34	13.82	13.74
1.5	25.53	23.49	18.08	24.21	18.71	18.96	20.33	17.63	17.28	24.25	20.86	16.57
2	26.9	24.88	21.8	25.3	23.81	19.7	20.93	19.33	18.79	25.2	21.66	19.54
2.5	27.51	25.61	22.75	25.73	24.66	24.43	22.36	21.36	22.12	26.46	22.74	19.91
3	29.03	26.27	24.86	26.45	24.67	24.6	24.7	21.66	22.81	27.09	25.54	24.44

Fastness properties: Fastness properties of intermediate dyes and anti-UV dyes (T1-T3, Dye1-Dye9) are shown in Table 5. Results show very good fastness properties for crocking 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 5. Fastness properties of 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	2-3	3	3	2-3	3	3	2-3	3	3	5-6
Dye1	4-5	4-5	3	3-4	3	3	3-4	3	3	4	4	6
Dye2	4-5	4	3-4	4-5	4	3-4	4	4	3-4	4	4	6-7
Dye3	4-5	4-5	3-4	4-5	4	3-4	4	4	3-4	4	4	6-7
T2	4-5	4	3	3-4	3	2-3	3	3	2-3	2-3	2	5-6
Dye4	4-5	4	4-5	4-5	4	4	4	4	4-5	4-5	4	6
Dye5	4-5	4	4-5	4-5	4	4-5	4-5	4	4-5	4	4	6-7
Dye6	4-5	4	4-5	4-5	4	4-5	4-5	4	4-5	4	4	6-7
T3	4-5	4-5	2-3	3	3	2-3	3	3	2-3	3	3	5-6
Dye7	4-5	4-5	3	4-5	3	3	4	4	4	4	4	6
Dye8	4-5	4-5	3-4	4-5	4	3	4	4	4	4	4	6-7
Dye9	4-5	4-5	3-4	4-5	4	3	4	4	4	4	4	6-7

St.* = Staining on cotton

St.**= Staining on wool

Alt. = Alteration in color

The total color difference (ΔE): From Table 6, it can be observed that with increasing time of irradiation of dyed nylon 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 $\text{NO}_2 > \text{Cl} > \text{Br}$ groups.

The rate of fading for nylon samples dyed with Dye1-9 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 Dye1-3, 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 presence of carbonyl group in 2,4-dihydroxy benzophenone in Dye2, Dye5 and Dye8.

TABLE 6. The rate of fading of nylon fabric dyed with dye intermediates (T1-T3) and anti-UV azo dyes (1-9).

Time of Irradiation In hr		T1	Dye1	Dye2	Dye3	T2	Dye4	Dye5	Dye6	T3	Dye7	Dye8	Dye9
0hr	L	50.55	31.59	33.54	29.28	38.09	32.33	31.6	28.4	46.62	30.40	31.00	29.50
	a	22.85	36.87	33.80	34.53	25.73	26.38	29.66	30.32	34.46	36.37	33.67	32.51
	b	21.06	13.08	16.54	13.34	20.28	22.46	17.82	15.35	37.87	17.48	20.66	16.82
	ΔE	59.34	51.78	50.41	47.20	50.24	47.58	47.04	44.29	60.53	50.52	50.22	47.02
35hr	L	53.58	35.07	33.79	29.27	34.42	33.09	31.81	28.9	48.73	34.95	38.73	34.02
	a	19.12	34.44	33.98	34.91	31.61	25.21	25.58	29.77	24.60	32.29	30.15	31.03
	b	17.85	20.21	17.15	13.83	18.75	21.45	20.42	16.01	25.06	21.88	18.08	15.60
	ΔE	59.63	53.15	51.10	47.61	50.65	47.06	45.64	44.48	61.47	52.37	52.31	48.62
70hr	L	45.48	44.03	40.70	29.63	42.53	35.31	33.86	30.25	50.47	38.65	35.96	38.10
	a	17.75	26.94	29.83	34.84	22.78	24.21	24.47	27.88	22.72	29.96	33.25	28.38
	b	16.62	18.07	18.77	13.76	19.42	21.49	21.36	20.05	24.04	21.53	18.58	15.01
	ΔE	59.66	54.69	53.84	47.76	52.00	48.34	46.92	45.77	62.56	53.43	52.38	49.82
105hr	L	47.64	48.19	47.86	30.59	48.17	32.92	37.44	29.53	46.07	42.11	44.61	41.77
	a	26.82	24.12	22.93	35.19	18.79	27.35	24.38	30.54	29.10	27.67	25.13	25.17
	b	25.03	17.65	16.22	14.43	17.89	23.45	17.94	16.07	30.14	20.19	15.39	14.18
	ΔE	60.13	56.71	55.50	48.81	54.71	48.91	48.14	45.42	62.93	54.28	53.47	50.77
140hr	L	44.52	51.05	44.30	30.59	49.3	32.00	37.81	29.76	48.63	45.35	46.07	47.72
	a	31.07	21.37	27.57	35.19	17.42	29.77	22.62	29.59	26.79	23.90	22.71	19.35
	b	31.53	16.47	19.00	14.43	16.62	22.68	21.84	16.5	28.74	18.29	15.01	12.32
	ΔE	62.78	57.74	55.53	48.81	54.71	49.5	49.17	45.33	64.61	54.43	53.51	53.06
175hr	L	45.68	55.10	47.98	31.31	56.60	42.12	43.78	31.09	45.46	46.16	47.06	46.42
	a	36.22	17.24	23.10	34.70	12.15	30.55	17.42	30.59	36.63	23.23	22.07	22.67
	b	44.89	13.83	16.72	14.45	12.86	26.2	19.21	17.7	44.40	18.01	14.51	13.92
	ΔE	73.35	59.37	55.82	48.92	59.3	52.33	50.89	47.07	73.58	54.72	53.97	53.50

Conclusion

Novel nine azo dyes containing anti-UV absorbers (anti-UV dyes) were prepared using primary aromatic amines (P.No₂, Cl, Br aniline) and J – acid coupler. Resorcinol, 2, 4- dihydroxy bezophenone and 1- hydroxyl benzotriazol 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 give the highest fading results.

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تشيد صبغات وظيفية مضادة للأشعة فوق البنفسجية وتطبيقاتها في صباغة الياف النيلون

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المركز القومى للبحوث – الجيزة* و كلية العلوم – جامعة بنها – بنها – مصر.

- تم تحضير تسعة من صبغات الأزو الجديدة التى تحتوى على مجموعات ماصة للأشعة فوق البنفسجية وذلك بتفاعل كل من (بارا كلورو، بارا برومو، بارا نيترو انلين) مع حمض الهيدروكلوريك و نيتريت الصوديوم فيعطى مركب الأزو الذى بدوره يتحد مع (J- acid) الذائبة فى كربونات الصوديوم لتعطى المركب الوسطى الذى بدوره يتفاعل مع حمض الهيدروكلوريك و نيتريت الصوديوم فيعطى مركب الأزو الذى بدوره يتحد مع المواد الماصة للأشعة فوق البنفسجية

(Resorcinol, 2, 4- dihydroxy benzophenone, 1- hydroxyl benzotriazol sulfonic acid).

- تم اثبات التركيب الكيميائى لهذه الصبغات عن طريق التحاليل الطيفية المعروفة

(IR, ¹H-NMR).

- تم استخدام هذه الصبغات فى صباغة الياف النيلون
- الاقمشة المصبغة بهذه الصبغات تم قياس لها كل من

- 1- شدة اللون
- 2- معدل البهتان
- 3- خواص الثبات