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# Light-stabilised Azo Dyes Containing a Built-in Ultraviolet Absorber Residue

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## *SUMMARY*

*2,4-Dihydroxybenzophenone is a commercially known ultraviolet absorber. The present paper deals with the study of azo dyes containing such an ultraviolet absorber incorporated into the dye chromophore. The effect of such an ultraviolet absorber on the fastness properties, particularly lightfastness, was studied by comparing these dyes with those made from resorcinol.*

## 1 INTRODUCTION

Ultraviolet absorbers are additives used to prevent photodegradation of polymeric materials by sunlight. In recent years, due to the increase in demand for coloured polymers, the problem of photodegradation of the polymers as well as the colorant has become important.

Recent patent specifications mention the incorporation of an ultraviolet absorber into a dye chromophore to obtain lightfast dyes for polypropylene fibres containing nickel.[1,2] An earlier report has also claimed the effectiveness of a UV absorber such as 4-amino-2-hydroxybenzophenone in the preparation of fibre-reactive dyes for cotton.[3]

This present investigation is concerned with incorporating the residue of an ultraviolet absorber into azo dyes for cotton, wool and leather. 2,4-Dihydroxybenzophenone, which has a reactive site for coupling, was utilised as coupling component with 4,4′-diaminostilbene-2,2′-disulphonic acid and

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3,3′-dichlorobenzidine as diazo components for direct and acid dyes respectively. By tetrazotising the diamine and coupling initially with pyrazolone, naphthylamine or naphthol derivatives and then with resorcinol or 2,4-dihydroxybenzophenone, two series of dyes were synthesised and compared with respect to their fastness properties, particularly lightfastness. It was anticipated that the dyes containing the UV absorber residue would give dyeings having better lightfastness and lead to deeper shades than the dyes derived from resorcinol.

## 2 RESULTS AND DISCUSSION

Direct dyes from 4,4′-diaminostilbene-2,2′-disulphonic acid (utilized as a possible alternative to benzidine) were prepared by tetrazotising the diamine and coupling with H-acid, J-acid, 1-(4-sulphophenyl)-3-carboxy-5-pyrazolone, NW-acid and Gamma acid respectively and then with resorcinol or with 2,4-dihydroxybenzophenone. The resultant dyes are typified by structures **I–V**.

All the dyes containing the benzoyl group, i.e. those derived from 2,4-dihydroxybenzophenone, gave dyeings with deeper shades on cotton than the dyes from resorcinol. The dyes did not give complete dyebath exhaustion, but whilst there was no significant difference in the washfastness of the dyes from each series, an increase of 1–2 units in the lightfastness was apparent with the dyes derived from 2,4-dihydroxybenzophenone.

In the case of dye **IIIb** derived from 1-(*N*-sulphophenyl)-3-carboxy-5-pyrazolone and 2,4-dihydroxybenzophenone a rather unusual bordeaux shade was obtained compared to the light scarlet shade given by dye **IIIa** derived from resorcinol. The various couplers used, visible absorption maxima of the resultant dyes, hues of the dyes obtained on cotton and their fastness properties are given in Table 1.

The water-soluble dyes from resorcinol and 2,4-dihydroxybenzophenone were also applied to leather and showed good exhaustion. Table 2 gives a preliminary evaluation of some of these dyes on leather.

In a similar manner, dyes were synthesised from 3,3′-dichlorobenzidine. The diamine was tetrazotised and coupled initially with H-acid, naphthionic acid and Gamma-acid respectively and then with resorcinol or 2,4-dihydroxybenzophenone to give dyes typified by structures **VI–VIII**. Whilst the dyes derived from 2,4-dihydroxybenzophenone did not show significant increase in washfastness, lightfastness was again higher by 1–2 units in all cases. Although the dyeings were not bright, deeper shades were obtained from the dyes containing the benzoyl group.

The various couplers used, hues of the dyes obtained on wool, visible

**TABLE 1**
Properties of the Dyes I–V

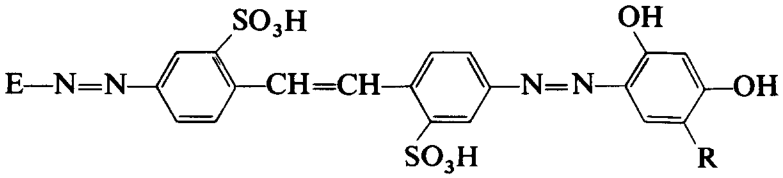
| *Dye* | *E* | *R* | $\lambda_{max}$[a] (*nm*) | *Shade on cotton* | *Dyeing properties*[b] | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | *PU* | *LF* | *WF* | *SC* | *SW* |
| **Ia** | H-acid | H | 510 | Violet | 1/6 | 2 | 3–4 | 4–5 | 4–5 |
| **b** | H-acid | $-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{Ph}$ | 580 | Greenish blue | 1/6 | 3–4 | 4 | 4–5 | 4–5 |
| **IIa** | J-acid | H | 510 | Reddish violet | 1/6 | 2 | 4 | 4–5 | 4 |
| **b** | J-acid | $-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{Ph}$ | 536 | Bluish violet | 1/3 | 3 | 4–5 | 4–5 | 4–5 |
| **IIIa** | 3-Carboxy-*N*-(*p*-sulphophenyl)-5-pyrazolone | H | 492 | Light scarlet | 1/6 | 1–2 | 3–4 | 4–5 | 4–5 |
| **b** | 3-Carboxy-*N*-(*p*-sulphophenyl)-5-pyrazolone | $-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{Ph}$ | 520 | Bordeaux | 1/3 | 3 | 3–4 | 4 | 4–5 |
| **IVa** | NW-acid | H | 524 | Reddish violet | 1/6 | 2 | 4–5 | 4 | 4–5 |
| **b** | NW-acid | $-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{Ph}$ | 540 | Bluish violet | 1/6 | 3–4 | 4 | 3–4 | 3–4 |
| **Va** | Gamma acid | H | 500 | Reddish violet | 1/6 | 3 | 3 | 4–5 | 4 |
| **b** | Gamma acid | $-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{Ph}$ | 536 | Bluish violet | 1/3 | 4 | 3–4 | 4–5 | 4 |

[a] $\lambda_{max}$, visible absorption maximum (in 10% aq. $Na_2CO_3$). The dyes used in recording the visible spectra and in dyeing were resalted and the purity was checked by thin layer chromatography using the following solvents system: 4·0 ml *n*-butanol, 1·5 ml ethanol, 2·0 ml 28% aqueous ammonia, 2·0 ml pyridine and 1·5 ml water.

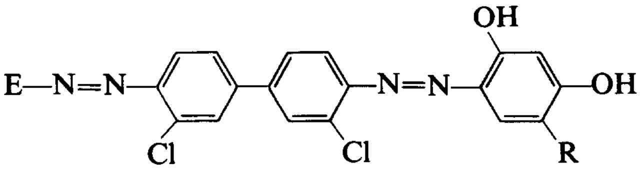
[b] PU, pick-up; LF, lightfastness; WF, washfastness; SC, staining on cotton; SW, staining on wool.

TABLE 2
Evaluation of Dyes **I**, **III** and **V** on Leather

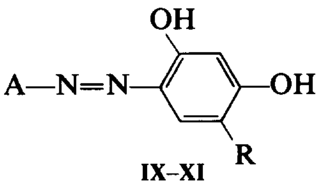
| *Dye* | *E* | *R* | *Shade on leather* | *Exhaustion* |
|---|---|---|---|---|
| **Ia** | H-acid | H | Violetish grey | Good |
| **b** | H-acid | $-\underset{\underset{\displaystyle O}{\|}}{C}-\mathrm{Ph}$ | Greenish blue | Good |
| **IIIa** | 3-Carboxy-*N*-(*p*-sulphophenyl)-5-pyrazolone | H | Orange | Good |
| **b** | 3-Carboxy-*N*-(*p*-sulphophenyl)-5-pyrazolone | $-\underset{\underset{\displaystyle O}{\|}}{C}-\mathrm{Ph}$ | Violet | Good |
| **Va** | Gamma acid | H | Reddish brown | Good |
| **b** | Gamma acid | $-\underset{\underset{\displaystyle O}{\|}}{C}-\mathrm{Ph}$ | Violet brown | Good |



**I–V**



**VI–VIII**



**IX–XI**

E = coupling component residue (see tables)

A = diazo component residue (see tables)

R = (**a**) H or (**b**)

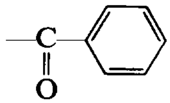
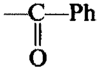
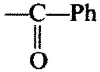
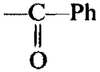


TABLE 3
Properties of the Dyes **VI–VIII**

| *Dye* | *E* | *R* | $\lambda_{max}$[a] (*nm*) | *Shade on wool* | *Dyeing properties*[b] | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | *PU* | *LF* | *WF* | *SC* | *SW* |
| **VI a** | H-acid | H | 560 | Reddish violet | 1/6 | 2–3 | 2–3 | 3–4 | 4 |
| **b** | H-acid | $-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{Ph}$ | 564 | Bluish violet | 1/6 | 3–4 | 2 | 3–4 | 4 |
| **VII a** | Naphthionic acid | H | 464 | Brick red | 1/3 | 3 | 3 | 2 | 3 |
| **b** | Naphthionic acid | $-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{Ph}$ | 490 | Light scarlet | 1/6 | 4 | 3 | 2–3 | 3–4 |
| **VIII a** | Gamma acid | H | 480 | Maroon | 1/3 | 2–3 | 2 | 2–3 | 3–4 |
| **b** | Gamma acid | $-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{Ph}$ | 500 | Reddish violet | 1 | 3–4 | 1–2 | 2–3 | 4 |

[a,b] Abbreviations as in Table 1.

## TABLE 4
Properties of the Dyes **IX–XI**

| *Dye* | *A* | *R* | $\lambda_{max}$[a] (*nm*) | *Shade on wool* | *Dyeing properties*[b] | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | *PU* | *LF* | *WF* | *SC* | *SW* |
| **IXa** | Sulphanilic acid | H | 424 | Yellowish brown | 1/1 | 3–4 | 2 | 4 | 4 |
| **b** | Sulphanilic acid |  $-\underset{\overset{\|}{O}}{C}-\mathrm{Ph}$ | 430 | Yellowish orange | 1/1 | 5 | 2 | 3–4 | 4 |
| **Xa** | Naphthionic acid | H | 456 | Yellowish brown | 1/1 | 4 | 1–2 | 3 | 4 |
| **b** | Naphthionic acid |  $-\underset{\overset{\|}{O}}{C}-\mathrm{Ph}$ | 484 | Reddish brown | 1/1 | 5 | 2 | 3 | 4 |
| **XIa** | *p*-Aminoazobenzene-sulphonic acid | H | 480 | Yellowish orange | 1/1 | 4 | 2–3 | 3 | 3–4 |
| **b** | *p*-Aminoazobenzene-sulphonic acid |  $-\underset{\overset{\|}{O}}{C}-\mathrm{Ph}$ | 500 | Reddish orange | 1/1 | 5 | 2–3 | 3 | 3 |

[a,b] Abbreviations as in Table 1.

absorption maxima of the dyes and their fastness properties are given in Table 3.

Monoazo dyes were also prepared by diazotising sulphanilic acid, naphthionic acid and *p*-aminoazobenzenesulphonic acid respectively and coupling with resorcinol or with 2,4-dihydroxybenzophenone. The resultant dyes, typified by structures **IX**–**XI**, gave very bright shades on wool and had good exhausting properties with consistently good pick-up values. No significant differences in washfastness were observed but all the dyes prepared from 2,4-dihydroxybenzophenone gave deeper shades and dyeings having better lightfastness than the corresponding dyes derived from resorcinol. Table 4 gives the various diazo components used, hues of the dyes obtained on wool, visible absorption maxima of the dyes and their fastness properties.

The results thus demonstrate the advantageous use of 2,4-dihydroxybenzophenone as a coupling component in both acid and direct dyes having improved fastness to light relative to analogous dyes derived from resorcinol.

## 3 EXPERIMENTAL

Visible spectra were recorded using a Uvikon spectrophotometer. 2,4-Dihydroxybenzophenone was prepared by benzoylating resorcinol (see for example refs 4–8).

### 3.1 Preparation of the disazo dyes I–V

A solution of 4,4′-diaminostilbene-2,2′-disulphonic acid (DASDS) (96%, 3·90 g, 0·01 mol) in water (50 ml) containing sodium carbonate (20%, 9 ml) was cooled to 0°C and treated with sodium nitrite (1·51 g, 0·022 mol). The solution was then added to 10% hydrochloric acid (21·9 ml) and tetrazotised at 0·5°C. Excess of nitrous acid was destroyed by adding urea. To the resultant solution was added a solution of the first coupler $E_1$ (0·01 mol) dissolved in the appropriate amount of aqueous sodium carbonate at 5–8°C. The pH of the reaction mixture was adjusted depending on the site of coupling and the mixture was stirred for 2–3 h (until a test solution on filter paper gave no blue colouration with H-acid solution).

#### *3.1.1 With resorcinol* (**a**)

A solution of the monoazo diazo solution described above (equivalent to 0·005 mol) was treated with resorcinol (0·55 g, 0·005 mol) dissolved in 10% sodium hydroxide (5 ml) and the mixture stirred at pH 8·5 and 8–10°C for

1 h. The dye was isolated by addition of salt (15% w/v) at 80°C. The dye was filtered and dried and resalted.

### *3.1.2 With 2,4-dihydroxybenzophenone* (**b**)

A solution of the monoazo diazo solution described above (equivalent to 0·005 mol) was treated with 2,4-dihydroxybenzophenone (1·07 g, 0·005 mol) dissolved in 10% sodium hydroxide (8 ml) and the mixture stirred at 8–10°C and pH 8·0–9·0 for 1 h. The dye was salted out (15% salt w/v) at 80°C and purified by resalting.

### 3.2 Preparation of disazo dyes VI–VIII

A solution of 3,3′-dichlorobenzidine sulphate (57·7%, 4·47 g, 0·01 mol) in 10% hydrochloric acid (22 ml) was stirred overnight and tetrazotised with sodium nitrite (1·5 g, 0·022 mol). Excess of nitrous acid was destroyed with urea.

A solution of coupler $E_1$ (Table 3) (0·01 mol) in aq. sodium carbonate was added to the tetrazotised solution and the mixture stirred at 5–8°C at a pH of 2–3 (in case of dye **VI**, at pH 8–8·5) for 3–4 h.

The second coupling was carried out by treating the above monoazo diazo solution (equivalent to 0·005 mol) with either resorcinol (0·55 g, 0·005 mol) or with 2,4-dihydroxybenzophenone (1·07 g, 0·005 mol) at pH 8–9 and 8–10°C for 1 h. The dyes were salted out and purified by resalting.

### 3.3 Preparation of the dyes IX–XI

The appropriate aromatic amine (0·01 mol) was diazotised at 0–5°C and coupled with resorcinol (0·01 mol) or with 2,4-dihydroxybenzophenone (0·01 mol) at pH 8·0 and 8–10°C for 1 h. The precipitated dye was filtered and dried.

## 4 CONCLUSION

Unsymmetrical azo dyes were prepared using resorcinol and 2,4-dihydroxybenzophenone as the end couplers. The dyes from 2,4-dihydroxybenzophenone gave dyeings having deeper shades and better lightfastness than those from resorcinol, in accordance with the anticipated results.

The dyes from 4,4′-diaminostilbene-2,2′-disulphonic acid had relatively poor exhaustion compared with acid dyes from 3,3′-dichlorobenzidine. No significant change in washfastness was observed in either case by introduction of the benzoyl group into the dye structure.

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