Comparison of Fixation Characteristics of New Acid Fixing Reactive 
Dyes Derived from 5, 10-Phenophosphazine Ring with 
Commercial Reactive Dyes on Nylon 66 and Wool Substrates

A Mamuda, K A Bello and M K Yakubu*

Department of Textile Science and Technology, A B U Zaria, Nigeria
Received: 08 October 2001; accepted: 22 May 2002

The traditional alkaline reactive dyes were found unsuitable for the continuous dyeing of the polyester/cotton blends. This and other problems lead to the search for the acid fixing reactive dyes. Calcobond and Procion T dyes were thus introduced. However, these series of dyes have suffered diminishing acceptability because of the expensive application conditions. Dyes derived from the 5,10-phenophosphazine ring were accidentally found to form covalent bonds with cellulose at neutral pH earlier. This report extends application of these groups of dyes to wool and nylon substrates. The effect of pH on exhaustion and fixation was investigated. The kinetics of dyeing was also studied and compared with some commercial alkaline fixing reactive dyes. The dyes have been established to be acid fixing on wool and nylon. A reaction mechanism has also been proposed.

Introduction

Reactive dyeing systems have become the most important discovery in the Colouration industry in the last century. Ever since they were discovered, diminishing era for the demand of other dye classes set in. Their major advantages are superior wet fastness properties and high brightness of colours. The earlier dyes produced are, however, fixed on to the substrates by an alkaline treatment at times at higher temperatures. As a result, they form either esters or ethers with cellulose. Later these dyes were found to have the following three disadvantages: (i) Lot of dye wastages due to hydrolysis, (ii) Could not be applied to cellulose/polyester blends as the disperse dye meant for the polyester component was decomposed at the temperature of application, and (iii) Due to the high alkalinity required some could not be applied unto wool and nylon substrates.

Researchers later introduced another group of reactive dyes that could fix onto the substrates by an acid fixing mechanism. The first group was introduced as calcobond and the second group as Procion T dyes. However, these dyes have now become obsolete. Their major disadvantage is the very drastic conditions needed to apply them. In certain cases, specialized equipment, i.e. baking units have to be employed. They also cannot be applied by exhaustion dyeing methods. Bello and Zhao stumbled into the 5, 10-phenophosphazine ring dye systems which they accidentally discovered to form covalent bond under neutral conditions with cellulose. Present study explores the possibility of the applicability of this system into the area of wool and nylon substrates.

The overall efficiency of any reactive dyeing systems depends on the following three factors: (i) Diffusion, (ii) Adsorption, and (iii) Fixation. These not only determine the fixation efficiency but also other important factors such as the levelness and to a certain extent the depth of penetration of the dye. The rate at which the hydrolysed dye is washed off is also governed by the diffusion rate. For this reason, a very efficient reactive dye is one that has just the minimum amount of affinity and as a consequence high diffusion coefficient, which would increase the washoff of the hydrolysed dye.

Diffusion attribute of reactive dyes is a very important property and has been given due attention by various workers. Diffusion is an indirect measure of the substantivity. High substantivity means low diffusion and vice versa. Capponi and Senn plotted relative diffusion coefficient against exhaustion curves. The change of substantivity with temperature was found to be inverse to the change of reactivity and diffusion with tempera-
ture. As a consequence, it was shown that the amount of dyestuff adsorbed by the fibre decreased with increase in temperature. However, the diffusion coefficient under reactive dyeing condition is difficult to compute since the dye reacts with the alkaline or acidic medium as well.

**Experimental Procedure**

*Determination of \( \lambda_{\text{max}} \)*

A Corning colorimeter 253 was used for the determination of the wavelength of maximum absorption of the dyes. The solutions were diluted with distilled water. The wavelength was varied at 2 nm interval from 400 nm to 700 nm and the absorbance noted. The extinction coefficient was then calculated at this \( \lambda_{\text{max}} \) using the Beers-Lambert's relation. The results are shown in Table 1.

*Dyeing Procedure*

All dyeings were carried out using 1 per cent (owf) at various pH described by MacInVaine buffer solution\(^7\). The substrate each was entered at 30 °C and boiled for 15 min at higher temperature and dyed at the boiling temperature for 60 min. The liquor ratio was maintained at 50:1. At the end of the dyeing the dyed samples were rinsed thoroughly in both warm and cold water and then dried.

The degree of exhaustion was determined by comparing the absorbance of the dye solution before and after dyeing, after making the necessary dilution and cooling.

**Determination of Dye Fixation.**

The dyed samples 0.5 g each, were stripped in 25 mL of 10 per cent pyridine solution under reflux for 1h. The solution was then cooled and made up to 50 mL. The absorbance was determined at the \( \lambda_{\text{max}} \) of the dye solutions. The amount of dye extracted was then extrapolated from a calibration curve of the pyridine/dye solution\(^8\).

The fixation efficiency was calculated as:

\[
\text{Per cent } T = \frac{\text{Dye in the substrate after stripping}}{\text{Dye in the original dye solution}}
\]

The results are shown in Table 2.

**Determination of Wash Fastness Properties**

Samples of the dyed fabrics at the various pH described above were used for this analysis. The dried

---

<table>
<thead>
<tr>
<th>Code</th>
<th>( \lambda_{\text{max}} )</th>
<th>( \varepsilon \times 10^4 )</th>
<th>Colour in water</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \lambda_{\text{max}} )</td>
<td>( \varepsilon \times 10^4 )</td>
<td>Colour in water</td>
<td></td>
</tr>
<tr>
<td>( \lambda_{\text{max}} )</td>
<td>( \varepsilon \times 10^4 )</td>
<td>Colour in water</td>
<td></td>
</tr>
<tr>
<td>( \lambda_{\text{max}} )</td>
<td>( \varepsilon \times 10^4 )</td>
<td>Colour in water</td>
<td></td>
</tr>
<tr>
<td>( \lambda_{\text{max}} )</td>
<td>( \varepsilon \times 10^4 )</td>
<td>Colour in water</td>
<td></td>
</tr>
</tbody>
</table>

Table 1—Visible absorption properties of the new dyes

<table>
<thead>
<tr>
<th>Code</th>
<th>( \lambda_{\text{max}} )</th>
<th>( \varepsilon \times 10^4 )</th>
<th>Colour in water</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \lambda_{\text{max}} )</td>
<td>( \varepsilon \times 10^4 )</td>
<td>Colour in water</td>
<td></td>
</tr>
<tr>
<td>( \lambda_{\text{max}} )</td>
<td>( \varepsilon \times 10^4 )</td>
<td>Colour in water</td>
<td></td>
</tr>
<tr>
<td>( \lambda_{\text{max}} )</td>
<td>( \varepsilon \times 10^4 )</td>
<td>Colour in water</td>
<td></td>
</tr>
</tbody>
</table>

Table 2—Fixation efficiencies of the dyes on nylon 66 and wool at various pH

<table>
<thead>
<tr>
<th>Dye</th>
<th>( \lambda_{\text{max}} )</th>
<th>( \varepsilon \times 10^4 )</th>
<th>Colour in water</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \lambda_{\text{max}} )</td>
<td>( \varepsilon \times 10^4 )</td>
<td>Colour in water</td>
<td></td>
</tr>
<tr>
<td>( \lambda_{\text{max}} )</td>
<td>( \varepsilon \times 10^4 )</td>
<td>Colour in water</td>
<td></td>
</tr>
<tr>
<td>( \lambda_{\text{max}} )</td>
<td>( \varepsilon \times 10^4 )</td>
<td>Colour in water</td>
<td></td>
</tr>
</tbody>
</table>

---

1. Corning colorimeter 253 was used for the determination of the wavelength of maximum absorption of the dyes.
2. The solutions were diluted with distilled water.
3. The absorbance was noted.
4. The extinction coefficient was then calculated at this \( \lambda_{\text{max}} \) using the Beers-Lambert's relation.
5. The results are shown in Table 1.
6. All dyeings were carried out using 1 per cent (owf) at various pH described by MacInVaine buffer solution.
7. The substrate each was entered at 30 °C and boiled for 15 min at higher temperature and dyed at the boiling temperature for 60 min.
8. The liquor ratio was maintained at 50:1.
9. At the end of the dyeing the dyed samples were rinsed thoroughly in both warm and cold water and then dried.
10. The degree of exhaustion was determined by comparing the absorbance of the dye solution before and after dyeing, after making the necessary dilution and cooling.
11. The dyed samples 0.5 g each, were stripped in 25 mL of 10 per cent pyridine solution under reflux for 1h.
12. The solution was then cooled and made up to 50 mL.
13. The absorbance was determined at the \( \lambda_{\text{max}} \) of the dye solutions.
14. The amount of dye extracted was then extrapolated from a calibration curve of the pyridine/dye solution.
15. The fixation efficiency was calculated as:

\[
\text{Per cent } T = \frac{\text{Dye in the substrate after stripping}}{\text{Dye in the original dye solution}}
\]

The results are shown in Table 2.
16. Samples of the dyed fabrics at the various pH described above were used for this analysis.
17. The dried samples were treated with the specified fixation conditions.
18. The fixation efficiencies were recorded.
19. The results are shown in Table 2.
samples were subjected to ISO3 wash fastness test. The results are given in Table 3.

**Determination of the Diffusion Coefficient**

Nine tightly-closed dyeing test tubes were placed in a thermostated dye bath set at 40° and 70°C. Dye liquor was placed in each to give 20 per cent shade and a liquor ratio of 20:1 at pH 7. Samples (0.5g) were placed in each test tube. Timing was started when the temperature of the dyeing liquor equilibrated with the bath and then a sample was removed at intervals of 5 min and the last sample removed after 5 h. The dyed sample was then washed and squeezed well with about 20 cm$^3$ of warm water. The washings were then transferred to the dyeing liquor. The dyeing liquor was then diluted with 100 cm$^3$ of water. 1 cm$^3$ of this was diluted to 10 cm$^3$. The absorbances of these solutions at 5 min intervals were the $C_i$ whereas that at 5 h was $C_{oo}$.

Graphs of $C/C_{oo}$ against $t^{1/2}$ were then plotted from where slopes were obtained. The diffusion coefficients were then calculated using Eq. (1)

$$D = \frac{(\text{Slope})^2 \pi}{4} \quad \ldots (1)$$

The results are given in Table 4.

**Determination of Activation Energy**

From the calculated diffusion coefficients at the two temperatures the activation energies of the dyes on the two substrates were then computed using Eq. (2).

$$E = 29738 \ln \left(\frac{D_{313K}}{D_{343K}}\right) \quad \ldots (2)$$

$D_{313K}$ and $D_{343K}$ are the diffusion coefficients at 343K and 313K, respectively.

**Table 3** - Wash fastness properties of the dyes on nylon 66 and wool substrates applied at the different pH conditions

<table>
<thead>
<tr>
<th>Dye</th>
<th>pH</th>
<th>N</th>
<th>W</th>
<th>N</th>
<th>W</th>
<th>N</th>
<th>W</th>
<th>N</th>
<th>W</th>
<th>N</th>
<th>W</th>
<th>N</th>
<th>W</th>
<th>N</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>2</td>
<td>5454</td>
<td>5454</td>
<td>5454</td>
<td>5454</td>
<td>5454</td>
<td>2222</td>
<td>2212</td>
<td>2221</td>
<td>2212</td>
<td>1212</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>5444</td>
<td>5454</td>
<td>4444</td>
<td>4444</td>
<td>4444</td>
<td>2222</td>
<td>2222</td>
<td>2222</td>
<td>2222</td>
<td>2222</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>4444</td>
<td>4444</td>
<td>4444</td>
<td>4444</td>
<td>3444</td>
<td>3333</td>
<td>3333</td>
<td>3333</td>
<td>3333</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>4344</td>
<td>4444</td>
<td>4434</td>
<td>4444</td>
<td>3434</td>
<td>3333</td>
<td>3333</td>
<td>3333</td>
<td>3333</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>3333</td>
<td>3333</td>
<td>3333</td>
<td>3333</td>
<td>3333</td>
<td>4444</td>
<td>4444</td>
<td>4444</td>
<td>4444</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>3233</td>
<td>3233</td>
<td>3233</td>
<td>3233</td>
<td>3233</td>
<td>3233</td>
<td>3233</td>
<td>3233</td>
<td>3233</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>3122</td>
<td>3122</td>
<td>3122</td>
<td>3122</td>
<td>3122</td>
<td>3122</td>
<td>3122</td>
<td>3122</td>
<td>3122</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

N is nylon 66, W is wool. The first number is charge in shade whereas the second is the degree of staining.

**Table 4** - Diffusion coefficient and activation energies of the dyes on nylon and wool substrates.

<table>
<thead>
<tr>
<th>Dye No.</th>
<th>Nylon</th>
<th>Diffusion coefficient/s at 313K</th>
<th>Activation energy, J/mol</th>
<th>Wool</th>
<th>Diffusion coefficient/s at 313K</th>
<th>Activation energy, J/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>1.1 x 10$^{-4}$</td>
<td>2.5 x 10$^{-4}$</td>
<td>24413</td>
<td>2.0 x 10$^{-4}$</td>
<td>3.1 x 10$^{-4}$</td>
<td>13033</td>
</tr>
<tr>
<td>1b</td>
<td>0.7 x 10$^{-4}$</td>
<td>1.1 x 10$^{-4}$</td>
<td>13441</td>
<td>0.9 x 10$^{-4}$</td>
<td>1.5 x 10$^{-4}$</td>
<td>15191</td>
</tr>
<tr>
<td>1c</td>
<td>2.0 x 10$^{-4}$</td>
<td>4.9 x 10$^{-4}$</td>
<td>26648</td>
<td>1.3 x 10$^{-4}$</td>
<td>2.5 x 10$^{-4}$</td>
<td>19446</td>
</tr>
<tr>
<td>1d</td>
<td>1.7 x 10$^{-4}$</td>
<td>3.4 x 10$^{-4}$</td>
<td>20613</td>
<td>1.1 x 10$^{-4}$</td>
<td>2.5 x 10$^{-4}$</td>
<td>24414</td>
</tr>
<tr>
<td>2a</td>
<td>1.51 x 10$^{-4}$</td>
<td>2.0 x 10$^{-4}$</td>
<td>8357</td>
<td>1.51 x 10$^{-4}$</td>
<td>2.0 x 10$^{-4}$</td>
<td>8357</td>
</tr>
<tr>
<td>2b</td>
<td>0.70 x 10$^{-4}$</td>
<td>1.5 x 10$^{-4}$</td>
<td>22665</td>
<td>0.9 x 10$^{-4}$</td>
<td>2.0 x 10$^{-4}$</td>
<td>23746</td>
</tr>
<tr>
<td>2c</td>
<td>0.90 x 10$^{-4}$</td>
<td>2.0 x 10$^{-4}$</td>
<td>23746</td>
<td>2.0 x 10$^{-4}$</td>
<td>3.1 x 10$^{-4}$</td>
<td>13033</td>
</tr>
<tr>
<td>2d</td>
<td>0.60 x 10$^{-4}$</td>
<td>1.5 x 10$^{-4}$</td>
<td>27249</td>
<td>0.7 x 10$^{-4}$</td>
<td>1.7 x 10$^{-4}$</td>
<td>26387</td>
</tr>
<tr>
<td>2e</td>
<td>0.60 x 10$^{-4}$</td>
<td>1.7 x 10$^{-4}$</td>
<td>30971</td>
<td>1.1 x 10$^{-4}$</td>
<td>1.5 x 10$^{-4}$</td>
<td>9223</td>
</tr>
</tbody>
</table>
The results are shown in Table 4.

Structures of the new dyes

![Structure diagram]

Commercial dyes used

(1) Procion orange H-2R (2a)
(2) Procion red H-3B (2b)
(3) Procion yellow H-5G (2c)
(4) Procion yellow MX-SB (2d)
(5) Procion red MX-8B (2e)

The new dyes were obtained from Key State Laboratory of dyes and surfactants, Dalian University of Technology, China and the commercial dyes were obtained from the University of Leeds, UK.

Results and Discussion

Lot of literature is available about the reactive sites on wool keratin that could react with groups in the dyes. The side chain is believed to contain -NH, -NH₂, -OH and -SH groups in abundance. One kg of wool contains about 1 equivalent of alcoholic -OH groups, 0.03 equivalent of -SH groups, 0.26 equivalent of phenolics, -OH groups, 0.16 equivalent of -NH groups. With acryl amide dyes the -SH groups were found to be accessible at pH 4, amino groups at pH 5. With more highly activated reactive dyes such as the dichloro triazine systems, reaction of the amino groups was possible at pH below 5. The amorphous region of the fibre is mostly reactive amino acids. It has been also shown that both primary and secondary amino groups reacted in weakly acidic medium.

The fixation data for the new dyes, shown in Table 2, clearly shows a decrease with increase in pH. Increase in fixation with decrease in pH is in consonance with acid dyeing mechanism of wool or nylon substrates. But increase in fixation with decrease in pH is only possible when acid-fixing mechanism is assumed. In most of the cases the higher exhaustion and fixation for wool substrate over the nylon material is maintained.

Among the commercial dyes, it is seen in Table 2, that the dichloro triazine dye (2e) has the highest fixation efficiency in the group. It is also observed that for this types of dyes both exhaustion and fixation increased with pH. Being alkaline fixing this could be anticipated.

When the two substrates are compared for all the dyes at almost all the pH values, exhaustion and fixation efficiencies on the wool substrates were higher than on the nylon material; this is a direct consequence of the amino end group present in the materials.

When the fixation data between the new and the commercial dyes are compared the new dyes are observed to record higher values. This gives additional advantage of the acid fixing reactive dyes. The unfixed dye is the hydrolysed one. The acid fixing reactive dye from this observation has lower waste or higher selectivity ratio. Further advantage of this new type of reactive dye is that the fixation is achieved by a simple exhaust method without the need of a baking unit or any condensing agent.

It is evident from Table 3 that the values for the wash fastness ratings of the new dyes are in conformity with acid fixing mechanism. It is seen that at acidic or lower pH values the wash fastness rating is found to be excellent as compared with the alkaline fixing types, which recorded higher ratings at the alkaline pH.

The proposed reaction mechanism for the fixation of the new dyes on to the substrate is given in Scheme 1.

Step 1 in Scheme 1 is possible because oxygen has higher electronegativity of 3.44 compared to only 2.19 in the case of phosphorus. This type of delocalization takes place even when oxygen is joined with carbon where the electronegativity of carbon is about 2.55 (ref. 12). The second step, involving protonation of the negatively charged oxygen atom is assumed to be the rate-determining step.

The significance of the diffusion coefficients especially that of the recorded values for the new dyes being higher than the commercial ones can be appreci-
ated when realized that the pH at which they were determined favoured the commercial dyes.

At this pH the commercial dyes had higher exhaustions than the new dyes. For example dye (1a) has exhaustion of 20 per cent at pH 7 whereas dye (2a) has about 45 per cent at the same pH level on nylon. However, these two respective dyes recorded 2.5 x 10⁴ 1/s and 2.0 x 10³ 1/s as diffusion coefficients at 343 K. It had been documented that the rate of dyeing increases with increase in exhaustion. In Table 4 the values of the activation energies show that the new dyes record lower values when compared with the dichloro triazine dyes (2d) and (2e) on nylon substrates.

However, with respect to the monochlorotriazine systems the difference is not so conclusive but the values are very similar. In general, subject to experimental errors the new dyes have acceptable kinetic properties when compared with the commercial dyes.

Conclusion
The new dyes have proved to be acid fixing. They recorded higher fixation and exhaustion data than the commercial alkaline fixing reactive dyes. This is attributed to lower hydrolysis and higher selectivity when compared with the commercial cyanuric chloride derived dyes. They also provide an advantage over the earlier calcein bond and procion T dyes in the sense that they have lower activation energy since they are fixable at lower temperatures without the need of any condensing or catalyzing agent other than acid.

References
8. Alhaji M Comparison of fixation characteristics of newly synthesized acid fixing reactive dyes derived from 5,10-phenophosphazine ring with commercial reactive dyes, MSc Thesis, Ahmadu Bello University, Zaria 2001.