Abstract: The process of clearing the excess disperse dye left on the surface of the polyester fibre cannot be avoided for most colours, since this dye will later stain adjacent fabric. An oxidative clearing process for disperse dyes, with hydrogen peroxide, was applied, substituting in this way a process which is usually applied, which is the reduction clear done with sodium hydrosulphite. This is a very polluting process, due to the high values of CQO and conductivity obtained as a result of its application. Besides the polluting aspects it also has better fastness than the alternative reduction clear sequence. If applied after dyeing it saves on time and water since it eliminates rinsing before dyeing. For PE/CO blends dyed with disperse/ reactive dyes it is necessary to protect the dyes to the attack of hydrogen peroxide free radicals. In this work a novel process of protecting the dyes with a product containing free radical quenchers was applied simultaneously with the peroxide. This treatment avoided hue alterations which occur otherwise when oxidative treatment is applied.

Introduction

The process of clearing the excess disperse dye left on the surface of the polyester fibre cannot be avoided for most colours, since this dye will later stain adjacent fabric. It can be avoided altogether, in certain circumstances, such as dyeing polyester in light colours, which can do without the clearing process since the amount of dye resting on the surface of the fibre which needs to be cleared is not enough to affect the fastness. These cases make up only a very small proportion of dyeings in most dyehouses.

The dyeing of cotton/polyester blends with reactive/disperse dyes involves many steps which are mainly rinsing operations to eliminate products such as hydrogen peroxide, used in bleaching, and sodium hydrosulphphite (hydros) used in a clearing process of disperse dyes applied to polyester (Reduction clearing). The elimination of these products are necessary since they affect the reactive dyes which are subsequently going to be applied in the dyeing of cotton. These extra steps however, waste water and add time to the total duration of the process, which in today’s competitive and ecologically sensitive environment is a drawback. The reduction clearing done with sodium hydrosulphphite is in itself a very polluting process, due to the high values of CQO and conductivity.
conductivity obtained as a result of its application.

In the last few years, products such as enzymes were introduced to eliminate hydrogen peroxide and save on rinsing and time, without affecting the dyeing. In this work an oxidative clearing process for disperse dyes, with hydrogen peroxide, was applied as an alternative to the reduction clear done with sodium hydrosulphite.

**Post-Bleaching**

In previous works it was shown that by Post-Bleaching with hydrogen peroxide, on polyester/cotton dyed with disperse/reactive dyes, was possible to save 20-30% in time and 30-40% in water.1,2

**Oxidative clearing**

For the Polyester component of the PE/CO blends, it was found that the Post-Bleaching of cotton would act as an oxidative clearing of the disperse dye in the Polyester component. It could substitute the Reduction clearing, with the same results in fastness, and in some cases better, such as was the case for some dyes with thermomigration fastness problems. The ecological advantages were found to be significant, expressed mainly through the conductivity values of the effluent, which are greatly reduced (table 1). Another advantage is the water saved through the elimination of rinsing operations (4 - 6 rinses) when doing oxidative clearing, for PE/CO blends.

The classical and the Post-Bleaching/Oxidative Clearing sequences applied are represented on fig. 1

![Fig. 1- Sequence of operations in the dyeing of PE/CO blends](image)

**Classical:** 1-bleach; 2- PE dyeing; 3- Reduction clearing; 4-CO dyeing; 5-soaping

**Oxidative clearing:** 2-PE dyeing; 4- CO dyeing; 5-Oxidative Clearing

**Peroxide attack**

One of the problems with Post-bleaching is that it is most effective in alkaline conditions and if applied after dyeing of the cotton component it might affect the dyes on the cotton. Since this is the most interesting situation for water saving, as seen in figure 1, it can only be applied when the dyes in the cotton component are resistant to oxidative alkaline conditions. Under these conditions free radicals are formed which can attack the chromophore and alter the colour of some dyes. To minimise the attack a commercial antioxidant which would act as a free radical quencher was tested on several reactive dyes in the laboratory so as to test their robustness for industrial application (table 1). For dyes very sensitive to alkaline conditions, such as vinylsulphone, sodium perborate should be used.
Experimental

Materials and equipment

The samples were of knitted fabric of polyester/cotton blends, 50% dyed polyester and 50% undyed cotton, and of 100% polyester. The disperse dyes were chosen from the Dianix range (Dystar) and the Terasil range (Ciba-Geigy). The clearing processes were carried out at L:R 1:10 in a machine with water and fabric movement, the Linitest (Heraeus), with the dyeing containers, since the clearing is also a physical process and should imitate as much as possible the conditions in industry. Stentering was done in a laboratory Werner-Mathis stenter at 150ºC for 5min. The washfastness tests were carried out in a Linitest (Heraeus) with the standard washfastness containers.

Clearing Processes:
The processes for clearing the disperse dyes were as follows:

- Process I:
  Reduction Clear:
  2ml/l caustic soda 50%
  2g/l sodium hydrosulphite
  Time: 20 min
  Temperature: 80ºC

- Process II:
  Oxidative Clearing:
  1,5g/l Hydrogen peroxide 130 v
  4 g/l Sodium carbonate
  2 g/l Nortex Fix 370
  Time: 20 min
  Temperature: 100ºC

- Process III:
  Oxidative Clearing:
  1,5g/l Hydrogen peroxide 130 v
  2 g/l Nortex Fix 370
  Time: 20 min
  Temperature: 100ºC

- Process IV:
  Oxidative Clearing:
  1,5g/l Sodium perborate
  2 g/l Nortex Fix 370
  Time: 20 min
  Temperature: 100ºC

The dyebath formulas with which the fabric had been dyed in industry were as follows:

Dyebath Formula A:
0,20% DIANIX Deep Blue K-R
0,37% DIANIX Orange K-3G
0,07% DIANIX Red K-3G

Dyebath Formula B:
0,21% TERASIL Yellow W-4G
0,6% TERASIL Red WBF 200%
0,7% TERASIL Red W-4BG

Dyebath Formula C:
0,28% TERASIL Yellow W-4G
2,4% TERASIL Red WBF 200%
2,1% TERASIL Red W-4BG

The difference in colour between the different dyeings was read in a Datacolor Spectraflash spectrophotometer using the CIElab colour difference formula.
A washfastness test which is generally used to assess the disperse dye fastness and also the efficiency of the clearing process, the ISO 105 C06 C2S, was applied to the dyed samples of polyester/cotton and the staining of the multifibre was measured in the spectrophotometer.

**Results**

Table 1. Values of ΔE between different treatments for monochlorotriazine dyes

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Oxidative Clearing</th>
<th>Oxidative Clearing with Quencher</th>
</tr>
</thead>
<tbody>
<tr>
<td>Procion Blue H-EXL</td>
<td>3.003</td>
<td>2.074</td>
</tr>
<tr>
<td>Procion Crimson H-EXL</td>
<td>-</td>
<td>0.320</td>
</tr>
<tr>
<td>Procion Navy H-EXL</td>
<td>1.485</td>
<td>0.925</td>
</tr>
<tr>
<td>Procion Yellow H-EXL</td>
<td>3.436</td>
<td>2.180</td>
</tr>
<tr>
<td>Procion Orange H-EXL</td>
<td>2.609</td>
<td>1.312</td>
</tr>
<tr>
<td>Procion Red Brown H-EXL</td>
<td>0.777</td>
<td>1.771</td>
</tr>
<tr>
<td>Procion Emerald H-EXL</td>
<td>0.895</td>
<td>0.830</td>
</tr>
<tr>
<td>Procion Royal H-EXL</td>
<td>2.012</td>
<td>1.539</td>
</tr>
<tr>
<td>Procion Saphire H-EXL</td>
<td>3.970</td>
<td>3.207</td>
</tr>
<tr>
<td>Procion Deep Red H-EXL</td>
<td>2.633</td>
<td>1.011</td>
</tr>
<tr>
<td>Procion Turquoise H-EXL</td>
<td>4.827</td>
<td>3.398</td>
</tr>
<tr>
<td>Procion Blue H-ERD</td>
<td>0.273</td>
<td>0.197</td>
</tr>
</tbody>
</table>

**Washfastness results**

The washfastness results to the ISO 105 C06 C2 standard test are on tables 2-4.

**Table 2.** Values of Staining (using the grey scale) after ISO 105 C06 C2 for dyebath formula A on PE/CO blend (50/50) after stentering

<table>
<thead>
<tr>
<th>Process</th>
<th>S.D.C. Multifibre Test Fabric</th>
<th>Acet</th>
<th>CO</th>
<th>Nylon</th>
<th>PE</th>
<th>Acryl</th>
<th>Wo</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td></td>
<td>5</td>
<td>2</td>
<td>3</td>
<td>4-5</td>
<td>4-5</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td></td>
<td>2-3</td>
<td>5</td>
<td>2-3</td>
<td>3</td>
<td>4-5</td>
<td>4-5</td>
</tr>
<tr>
<td>III</td>
<td></td>
<td>2</td>
<td>5</td>
<td>2</td>
<td>3</td>
<td>4-5</td>
<td>4-5</td>
</tr>
<tr>
<td>IV</td>
<td></td>
<td>2-3</td>
<td>5</td>
<td>2-3</td>
<td>3</td>
<td>4-5</td>
<td>4-5</td>
</tr>
</tbody>
</table>

**Table 3.** Values of Staining (using the grey scale) after ISO 105 C06 C2 for dyebath formula B on PE/CO blend (50/50) after stentering

<table>
<thead>
<tr>
<th>Process</th>
<th>S.D.C. Multifibre Test Fabric</th>
<th>Acet</th>
<th>CO</th>
<th>Nylon</th>
<th>PE</th>
<th>Acryl</th>
<th>Wo</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td></td>
<td>4</td>
<td>5</td>
<td>4</td>
<td>5</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td></td>
<td>3-4</td>
<td>5</td>
<td>4</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>III</td>
<td></td>
<td>4</td>
<td>5</td>
<td>4</td>
<td>4-5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>IV</td>
<td></td>
<td>4</td>
<td>5</td>
<td>4</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

**Table 4.** Values of Staining (using the grey scale) after ISO 105 C06 C2 for dyebath formula C on 100% polyester after stentering

<table>
<thead>
<tr>
<th>Process</th>
<th>S.D.C. Multifibre Test Fabric</th>
<th>Acet</th>
<th>Cott</th>
<th>Nylon</th>
<th>PE</th>
<th>Acryl</th>
<th>Wo</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td></td>
<td>3-4</td>
<td>4-5</td>
<td>3-4</td>
<td>4-5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>II</td>
<td></td>
<td>4</td>
<td>5</td>
<td>4</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>III</td>
<td></td>
<td>3-4</td>
<td>4-5</td>
<td>3-4</td>
<td>4-5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>IV</td>
<td></td>
<td>4</td>
<td>5</td>
<td>4</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>
For polyester/cotton blends, from tables 1 and 2 it can be seen that processes II with alkaline peroxide and IV with perborate, give better fastness results on this dyebath formula of low fastness dyes than the reduction clearing process (process I). For polyester/cotton blends, from tables 3 and 4, processes II with alkaline peroxide and IV with perborate give approximately the same results on this dyebath formula of high fastness dyes as the reduction clearing process (process I). For 100% polyester, the results as seen in tables 5 and 6 are clearly better in processes II and IV than the reduction clearing process (process I). Process III, with neutral hydrogen peroxide, gave the worse results, but even so acceptable for the high fastness dyes.

Conclusions

Oxidative Clearing was shown to be just as effective as reduction clearing when testing the fastness of the disperse dye. When applied after dyeing with reactive dyes, the hue of some dyes were affected, but it was possible with some triazine dyes to minimise this by applying simultaneously a free radical quencher. It is then possible to choose a tricromy of reactive dyes that will be suitable to submit to an oxidative clearing done at the end of the reactive dyeing process, thus saving water, time, energy and reducing pollution.

References


Acknowledgements: We thank Indinor, Indústrias Químicas SA, for supplying Nortex Fix 370, and FCT-ADI for financial support through the IC-PME programme