Ecofriendly dyeing of synthetic fibres

S D Deshpande
Sasmira's Institute of Man-made Textiles, Mumbai 400 025, India

Synthetic fibres, including polyester, nylon and acrylic fibres, account for nearly 46% of the total world-wide fibre consumption. Ecological consideration led to the significant developments in fibre production and their colouration techniques. Several new dyes and chemicals have been introduced to reduce the pollution load in the effluent. Recent developments in iron-based dyes and use of vinylsulphone dyes for nylon are reviewed.

Keywords: Acrylic, Bannded dyes, Dyeing, Ecofriendly dyeing, Iron-based dyes, Nylon, Polyester, Vinylsulphone dyes

1 Introduction

During the last four decades, the textile industry has witnessed phenomenal growth of synthetic fibres, many of which are being commonly used because of their affordability and excellent functionality. Natural fibres like cotton, wool and silk, which served mankind for many years, have been, to a greater extent, replaced by man-made fibres such as nylon, olefins and polyester. World-wide consumption of synthetic fibres constitutes 46% of the total textile fibre consumption (42000 tones in 1996) as shown in Fig. 1.

There are various factors that influence future fibre and fabric systems and their processing, such as less energy, less water requirement, less investment, etc. However, the environment-friendly production and processing of fibres and fabrics has gained greater significance today and it has brought about various changes in the production and processing techniques.

In apparels, polyester has considerably gained over other fibres because of its better easy care characteristics and wrinkle resistance. One of the largest markets for polyester lies in the blends with cellulosics. The high modulus and resilience of PET make polyester suitable as filling fibre for quilts, pillows and sleeping bags which can be laundered. Various innovative processing techniques have produced polyester with comfort of cotton, soft warmth of wool and glamour of silk.

A combination of excellent wear resistance, retention of good appearance, low carpet cost and better dyeing properties make polyamide an ideal material for carpet industry. It is also a principal material for women's hosiery and certain stretch fabrics specially due to its low elastic modulus compared to that of polyester. Acrylics have found wide use as wool replacement fibre in knitted apparel products, carpet and home furnishing.

Recent developments that have taken place in the dyeing of polyester, nylon and acrylic fibres, particularly in reference to ecological considerations, have been highlighted in this paper.

2 Trends in Fibre Production

Over the last seventy years, we have witnessed the growth of synthetic fibres starting with the synthesis of nylon 66 in 1940s, polyester and acrylic in 1950s and olefin fibres in 1960s. Introduction of specialty fibres like lycra spandex, which permitted us to manufacture first lightweight stretch fabrics for swimwear, lingerie and outwear, finds distinctive position in the modern textile technology. Development of low-temperature polymerization in 1960 led to the invention of aromatic polyamides for high temperature/flame-resistant textiles, viz. nomex.

![Fig. 1—World-wide fibre consumption](image-url)
fibres, like Kevlar aramid, were introduced. The following decades saw the development of modified engineered fibres like hydrophilic, low-pilling, flame-retardant, mass-coloured and silk-like hollow polyester fibres: differential dyeing; antistatic, flame-retardant and mass-coloured nylon fibres; water-absorbent, low-pilling, flame-retardant, bicomponent and differential dyeable acrylic fibres; and several other multifunctional fibres.

In the recent years, the environmental consideration has led to the production of fibres that exhibit excellent new properties, such as recyclability and biodegradability. It is possible to recycle the polyester waste to ingredients and then back to new products through a process called methanolysis effectively closing recycling loop. Recycling technologies for nylon are also advanced and waste carpets can be recycled. The conversion of acrylic fibres to ingredients and the subsequent recycling is not possible. Several other techniques have been developed for waste utilization. Many current production processes use metal catalysts for polymerization that can be harmful to environment. In case of polyester, antimony and cobalt catalysts are considered as hazardous. Similarly, there are number of chemicals and textile auxiliary products used in preparatory and dyeing of polyester and other fibres which pose various environmental problems. Two possible alternatives to fill the void created by the banned dyes and chemicals are as follows:

- To experiment and identify dyes and chemicals from the existing ones which do not come under the preview of any ban and try them as alternatives or substitutes.
- To experiment and create new substitutes for the banned dyes and chemicals.

The following disperse dyes available in India (list not complete) are not banned and are safe for polyester dyeing:

- CI Disperse Yellow 1,3,13,56,64 & 83
- CI Disperse Violet 1,4,8,33,35,63 & 99
- CI Disperse Red 1,4,5,11,13,17,54,54:1,60,73,82,91,92,118,159 & 167:1
- CI Disperse Orange 3,13,25,30,32,44 & 127
- CI Disperse Blue 3,7,23,26,26:1,31,35,56,72,79,79:1,83,87,94,109,129,149 & 183
- CI Disperse Green 9
- CI Disperse Brown 1 & 4:1
- CI Disperse Black 1 & 2

During polyester dyeing, chlorinated carriers should be avoided and the high BOD/COD acetic acid should be replaced by alternative products like Duracid. Safe disperse dyes with ecofriendly dispersing agents should be used.
3.2 Evaluation of Ecofriendly Dyeing

An ecofriendly dyeing of polyester is evaluated for fastness properties (Table 1) and heavy metal contents (Table 2). Polyester dyeing with safe disperse dye substitutes and other chemicals shows satisfactory fastness properties (Table 1). Table 2 indicates the amount of heavy metal(s) leached out into synthetic sweat solution from dyed samples. The results show that the majority of the values of heavy metal contents of polyester are within the eco-limits, except chromium content of polyester dyed with Disperse Orange 25 and Disperse Orange 61 and nickel content of polyester dyed with all five dyes.

3.3 Innovative Approach

Environmental requirements, related legislation and stricter eco-regulation in international marketing served as major driving force for innovations in both the dye manufacturing and dye application industries.

### Table 1—Banned disperse dyes and their alternatives with their fastness properties

<table>
<thead>
<tr>
<th>Disperse dye (C.I. Generic)</th>
<th>C.I. No.</th>
<th>Chemical class of dye</th>
<th>Hue on polyester</th>
<th>Fastness (ISO) to</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Light (Medium)</td>
<td>Washing (Alteration)</td>
</tr>
<tr>
<td>Yellow 7</td>
<td>26090</td>
<td>Disazo</td>
<td>Reddish yellow</td>
<td>6</td>
</tr>
<tr>
<td>Yellow 23</td>
<td>26070</td>
<td>Disazo</td>
<td>Reddish yellow</td>
<td>6.5</td>
</tr>
<tr>
<td>Blue 1</td>
<td>64500</td>
<td>Anthraquinone</td>
<td>Greenish blue</td>
<td>4</td>
</tr>
<tr>
<td>Blue 364</td>
<td>NA</td>
<td>Methine</td>
<td>Bright greenish</td>
<td>3.5</td>
</tr>
<tr>
<td>Blue 367</td>
<td>NA</td>
<td>Azo</td>
<td>Greenish blue</td>
<td>7</td>
</tr>
<tr>
<td>Red 151</td>
<td>NA</td>
<td>Disazo</td>
<td>Bright red</td>
<td>5</td>
</tr>
<tr>
<td>Red 334</td>
<td>12225</td>
<td>Monoazo</td>
<td>Bright red</td>
<td>5</td>
</tr>
<tr>
<td>Red 17</td>
<td>11110</td>
<td>Monoazo</td>
<td>Red</td>
<td>4.5</td>
</tr>
<tr>
<td>Red 94</td>
<td>NA</td>
<td>Anthraquinone</td>
<td>Bright red</td>
<td>7</td>
</tr>
<tr>
<td>Blue 3</td>
<td>61505</td>
<td>Anthraquinone</td>
<td>Bright blue</td>
<td>5</td>
</tr>
<tr>
<td>Blue 23</td>
<td>61545</td>
<td>Anthraquinone</td>
<td>Bright blue</td>
<td>5</td>
</tr>
<tr>
<td>Blue 7</td>
<td>62500</td>
<td>Anthraquinone</td>
<td>Greenish blue</td>
<td>4</td>
</tr>
<tr>
<td>Blue 83</td>
<td>NA</td>
<td>Anthraquinone</td>
<td>Blue</td>
<td>6.5</td>
</tr>
<tr>
<td>Blue 26</td>
<td>63305</td>
<td>Anthraquinone</td>
<td>Blue</td>
<td>4</td>
</tr>
<tr>
<td>Blue 31</td>
<td>64505</td>
<td>Anthraquinone</td>
<td>Blue</td>
<td>4</td>
</tr>
<tr>
<td>Yellow 56</td>
<td>NA</td>
<td>Disazo</td>
<td>Reddish yellow</td>
<td>6.6</td>
</tr>
<tr>
<td>Yellow 86</td>
<td>NA</td>
<td>Nitrodiphenylamine</td>
<td>Reddish yellow</td>
<td>7</td>
</tr>
<tr>
<td>Orange 53</td>
<td>NA</td>
<td>Monoazo</td>
<td>Bright reddish</td>
<td>5</td>
</tr>
</tbody>
</table>

### Table 2—Heavy metal content from sweat extracts of 5% dyed polyester

<table>
<thead>
<tr>
<th>Dye (C.I. Generic)</th>
<th>Amount of heavy metal, mg/kg of fabric</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Copper</td>
</tr>
<tr>
<td>Disperse Blue 94</td>
<td>2.345</td>
</tr>
<tr>
<td>Disperse Orange 25</td>
<td>1.815</td>
</tr>
<tr>
<td>Disperse Yellow 64</td>
<td>0.589</td>
</tr>
<tr>
<td>Disperse Orange 61</td>
<td>1.886</td>
</tr>
<tr>
<td>Disperse Red 92</td>
<td>0.897</td>
</tr>
</tbody>
</table>

Eco Limit (MST) 3.0 5.0 0.2 0.1
Such innovative dye application methods for polyester and other fibres include the dyeing in supercritical carbon dioxide and the plasma treatment.

3.3.1 Dyeing in Supercritical Carbon Dioxide

Joseph Jasper, Ciba, and the research group of the German North-West Textile Research Institute in Krefeld revealed a new method of dyeing from an environmentally safe solvent, supercritical carbon dioxide (SCO$_2$). The method was demonstrated at ITMA 1991.

The solvent SCO$_2$ shows ideal properties in that it is cheap, recyclable and extremely safe. The carbon dioxide used in such processes is obtained as byproduct from fermentation and ammonia synthesis and, therefore, does not add to pollution. The disadvantage of the process is the high pressure involved which requires special vessel engineering. How the gases and liquids are affected by the changes in pressure and temperature can be explained by the phase diagram (Fig. 2).

At critical point, if the gas is heated above its critical temperature it cannot be liquefied, however high is the applied pressure. In the case of carbon dioxide, the critical point is at $31^\circ C$ temperature and 7.3 Mpa pressure. Above the critical temperature, the gases retain the free mobility of the gaseous state but with the increase in pressure, density will increase toward that of a liquid. Such a highly compressed gas is termed as a supercritical fluid and these modulus combine the valuable properties of both liquid and gas. The fluid has remarkable penetration properties.

Two machines are currently available for dyeing polyester yarn in package form. A typical dyeing procedure involves the following steps:

- Set up the bath with goods and a charge of pure disperse dye.
- Run in SCO$_2$.
- Raise the temperature and pressure to $130^\circ C$ and 30 Mpa.
- Gradually reduce the pressure to reduce the solubility of the dye in SCO$_2$.
- Recover the carbon dioxide

The method claims 100% dye uptake and eliminates the need for reduction clearing.

The following disperse dyes are found suitable for dyeing due to their solubility in SCO$_2$ (ref. 13):

3.3.2 Plasma Treatment

Plasma includes ionized gases that contain ions, electrons, radicals, excited molecules and atoms. These ionized gases are electrically neutral and are generated by electric discharge, high frequency electromagnetic oscillation, high energy radiations (such as $\alpha$ and X-rays), etc.

Plasma technology finds application in a number of areas of textile processing. It improves dye uptake and adhesion to fabric lamination, and modifies fabric surface in such a manner that it becomes receptive. The most important aspect of plasma treatment is that being non-aqueous and non-solvent based, it does not have any problem of effluent treatment and so it is more ecofriendly. Low-temperature plasma for textile finishing has commercially been exploited by some textile companies. Toray in Japan has developed both continuous and batch systems for polyester fabrics. The treatment is aimed at enhancement of the colour depth on polyester fabrics, especially black. It also imparts high hydrophilicity and other useful properties. Commercial manufacturers of plasma treatment equipment require high technology to generate uniform plasma over a large surface and a
huge volume in reactor to maintain the vacuum. A plasma treatment machine for industrial application has been manufactured successfully in Russia.

4 Nylon Dyeing

Glass transition temperature of nylon 66 and nylon 6 in wet state being very low (below 20°C), the diffusion of dyes is easy in these fibres. Mainly, the acid, metal complex and disperse dyes are used for their coloration.

4.1 Selection of Dyes and Chemicals

The main pollutants present in the nylon exhaust dye liquor are unexhausted dye, acetic acid, dye fixing agents and heavy metallic compounds. Keeping in mind the red-listed and banned chemicals and dyes, their proper selection is vital for ecofriendly dyeing.

In place of acetic acid which is used for maintaining the pH in nylon dyeing, suitable substitute should be used. Even the use of formic acid in place of acetic acid can reduce biological oxygen demand (BOD) in the effluent. Leveling agents which contain chlorinated hydrocarbon or bleaching with active chlorine must be avoided to eliminate significant amount of AOX (activated carbon absorbable organo halogens) in the effluent. The dyes which are not carcinogenic, allergic and sensitive to skin should be used. Azo dyes having such harmful properties are already banned. The following dyes available in India (list not complete) are safe for nylon dyeing:

- CI Acid Yellow 1,11,17,25,36,42,59,73,76,99,114, 132,244 & 45
- CI Acid Orange 7,10A,74,80,82 & 86
- CI Acid Red 1,14,18,35,37,52,70,88,183,194,195 & 219
- CI Acid Blue 25,89,113 & 120
- CI Acid Green 1,9 & 20
- CI Acid Brown 45,48,345,348 & 349
- CI Acid Black 1,21,24,26,52,58,61,63,64,77,164 & 235

4.2 Heavy Metal Contamination

The presence of heavy metals in the effluent obtained after nylon dyeing is very detrimental to operation of the waste treatment system. Apart from this, the eco-limits for the presence of traces of heavy metals on the madeups are also very low. Therefore, it is necessary to know the sources of contamination of heavy metals. It is observed that in addition to the known source of heavy metal contamination like mordant and premetalized dyes, the data published by American Dyestuff Manufacturers Institute (ADMII) show that traces of metals are expected to be present in various dye classes itself as given in Table 3 (ref. 26).

4.3 Search for Safe Premetalized Dyes for Nylon

There seems to be considerable scope to develop iron and aluminum complexed dyes giving equivalent fastness properties of conventional chromium and copper complexed dyes as viable environmental alternatives.26-33

The National Textile Centre recently announced the synthesis of iron complexed formazon dyes by research chemists at North Carolina State University. Iron being a non-toxic metal, the dyes based on this chemistry are reported to have excellent light fastness on nylon and could replace the existing metal complex dyes. The use of iron salt in case of afterchroming of mordent dyes is also suggested. A representative example of 1:2 iron complex dye, developed by Clariant, is shown in Fig.3 (ref.32).

4.4 Nylon Dyeing with Vinylsulphone Reactive Dyes

Environment concerns regarding the use of premetalized dyes have created new interest in possible use of reactive dyes for nylon dyeing. This can give deeper dyeing due to the double addition of

<table>
<thead>
<tr>
<th>Metal</th>
<th>Acid</th>
<th>Basic</th>
<th>Direct</th>
<th>Disperse</th>
<th>Fibre reactive</th>
<th>Vat</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>1.4</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Cadmium</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Chromium</td>
<td>3.2</td>
<td>2.5</td>
<td>3.0</td>
<td>3.0</td>
<td>24</td>
<td>83</td>
</tr>
<tr>
<td>Cobalt</td>
<td>79</td>
<td>33</td>
<td>35</td>
<td>45</td>
<td>71</td>
<td>110</td>
</tr>
<tr>
<td>Copper</td>
<td>37</td>
<td>6.0</td>
<td>28</td>
<td>37</td>
<td>52</td>
<td>60</td>
</tr>
<tr>
<td>Lead</td>
<td>&lt;1</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>1.0</td>
</tr>
<tr>
<td>Mercury</td>
<td>&lt;1</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>1.0</td>
</tr>
<tr>
<td>Zinc</td>
<td>&lt;13</td>
<td>&lt;32</td>
<td>8.0</td>
<td>3.0</td>
<td>4.0</td>
<td>4.0</td>
</tr>
</tbody>
</table>
R = SO₂NH(CH₂)OMe

Fig. 3—Iron complexed premetallized dye (Clarient)

R = SO₂NH(CH₂)OMe

Fig. 4—Double addition reaction of vinylsulphone reactive dye with nylon

Table 4—Extent to which dyes are lost in exhaust and wash liquor

<table>
<thead>
<tr>
<th>Dye class</th>
<th>Amount of dye discharged in effluents, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct</td>
<td>5–20</td>
</tr>
<tr>
<td>Acid</td>
<td>7–20</td>
</tr>
<tr>
<td>Basic</td>
<td>2–3</td>
</tr>
<tr>
<td>Metal complex</td>
<td>2–5</td>
</tr>
<tr>
<td>Sulphur</td>
<td>30–40</td>
</tr>
<tr>
<td>Reactive</td>
<td>20–40</td>
</tr>
<tr>
<td>Disperse</td>
<td>1–20</td>
</tr>
<tr>
<td>Vat</td>
<td>5–20</td>
</tr>
</tbody>
</table>

The attention of researchers to develop disperse vinylsulphone reactive dyes and cationic vinylsulphonic dyes in place of sulphonated dyes.

5 Acrylic Dyeing

Acrylic fibres, which account for about 20% of total world synthetic fibre production, show wool-like feel, bulking value, chemical inertness, and resistance to weathering, molds and bacteria. Du Pont produced first acrylic fibre on pilot plant scale in 1950 from 100% acrylonitrile which was extremely difficult to dye. Considerable amount of research work was carried out to develop fibre suitable for dyeing with different classes of dyes. This fibre received more attention than any other fibre, and the dyeing problems were solved by developing modified fibre and special type of dyes and retarders.[34-40]

5.1 Selection of Dyes and Chemicals

As mentioned for polyester and nylon, the selection of proper dyes and chemicals are of great importance for ecofriendly acrylic dyeing. One positive aspect of acrylic dyeing from ecological point of view is 90–97% exhaustion of cationic dyes on acrylic fibre. Table 4 shows the amount of dye discharged in the effluents after dyeing with various types of dyes.

The following dyes available in India (list not complete) are safe for acrylic dyeing.[12]

- CI Basic Yellow 2,11,13,25 & 28
- CI Basic Orange 22
- CI Basic Red 13,14,18,22 & 29
- CI Basic Violet 7,14 & 16
- CI Basic Blue 13,54 & 146
- CI Basic Brown 1
- CI Black 36

To get the maximum exhaustion, which is important on acrylic fibre, proper selection of the dyeing technique after careful consideration of fibre saturation value, dye saturation factor and saturation factor of retarder is very important. Using dye saturation factor and fibre saturation value, it is possible to determine whether a particular dyeing recipe will cause over saturation of the fibre or not. Similarly, the saturation factor of the retarder, which is used for level dyeing, can also be considered in a similar manner to arrive at proper saturation limit of the dyeing. The fibre saturation values of certain acrylic fibres and the saturation factors of cationic dyes are given in Table 5. It is very important to dye...
acrylic fibres keeping in view the above technical data for the economy and less water pollution due to the less amount of dyes and chemicals in the effluent.

6 Conclusion
Environmental consideration has great impact on the production and colouration of synthetic fibres, namely polyester, nylon and acrylic fibres. It has led to the development of new fibre production, dyeing and processing techniques. Innovative ecofriendly methods like dyeing in supercritical carbon dioxide and plasma treatments are emerging. The research work to develop new dyes, like iron complex dyes for nylon, and safe ecofriendly chemicals for dyeing and processing of synthetic fibres is in progress.

References