New Dyeing Process

The Coloration of High Tenacity Polyamide Fabrics with Acid Dyes Using a New Continuous Dyeing Process

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Fabrics made from high modulus, high tenacity, low shrinkage polyamide fibers are stable against light and heat, have low dry heat shrinkage (3%), are fatigue resistant with good adhesion properties, have high tenacity with outstanding toughness and are resistant to degradation and mildew (if finish free). End uses include coated and protective fabrics, sewing threads, tapes, backpacks, boots, camera and videocomputer bags, hunting apparel and gear, indoor/outdoor furniture, soft sided luggage, golf and duffle bags, upholstery and apparel. A problem with the fibers has been that fabrics made from them are difficult to dye and print. A new alternative method is described.

Existing Methods

Pigment Dyeing

Fabrics made from high modulus, high tenacity, low shrinkage polyamide fibers, both the flat filament and the texturized filament types, are dyed and printed with pigment/resin systems. Pigment dyeing and printing methods are widely used but suffer the following drawbacks:

- Relatively poor crocking fastness
- Inferior wash and lightfastness
- Inferior handle
- Difficult to achieve deep and dark shades

Jig, Beam and Pad Roll Dyeing

Almost all high tenacity polyamide fabrics are dyed in open width to avoid cracking and creasing in dyeing machines such as jigs, on beams and in pad-roll machines (1). These dyeing processes are susceptible to several problems in dyeing uniformity including tailing towards the end of the fabric roll and side-center-side and face-to-back shading. These dyeing processes require judicious use of leveling agents, good control of temperature and time and temperature of dye addition which are laborious, time consuming and difficult factors to control, resulting in a substantial amount of seconds.

Continuous Dyeing

A newly developed continuous dyeing process based on the use of a 100% solvent system comprises padding the open width goods in a heated (high boiling point) solvent system containing the acid dye, curing at high temperatures, rinsing and drying. Only acid dyes capable of complete solubility in the solvent system can be used in the process. Other finishing agents—such as antistatic, soil release or flame retarding agents—can also be added into the dye/solvent system but they must be completely soluble and should not decompose or affect the final shade or the fastness properties of the acid dyes.

The main drawbacks of this process are economics, practicality and control. Furthermore, only a very limited number of agid dyes can be used in the process.

HTN Dyeing Process

The HTN Process is based on the discovery that fabrics constructed from high modulus, high tenacity, low shrinkage polyamide fibers can be continuously thermosol dyed with acid dyes to produce goods free from barliness, front-to-end tailing, side-center-side and other shading problems. The goods dyed by the process show superior overall fastness and physical properties. Since the use of solvents and high temperature atmospheric or pressurized steamers are avoided, fabrics can be dyed efficiently and economically into any shade required.

In the process, polyamide fabric is padded in open width with a specially formulated dye pad solution at ambient temperatures and squeezed to reduce the amount of wet pickup. The cold dye pad solution used in the process is capable of dissolving and permeating the acid dye inside the polyamide fiber. The bath is designed and formulated to provide a uniform film on the fabric and to saturate the individual fibers, including crossover points. The objective is to avoid dye exhaustion at the padding stage and to completely penetrate and fix the dye inside the fiber during the dry heat curing stage. Curing is performed in a thermosol heated oven using dry heat at temperatures ranging from about 175 to 230°C (347 to 446°F) for one to six minutes. The combination of padding under cold conditions and high temperature dry heat curing or thermosoling permits dyeing speeds of up to 200 yards per minute. Next, the fabric is cooled. Any undyed dyes and impurities are removed by rinsing and scouring. Lastly, the fabric is dried.

The process utilizes the same processing equipment—such as a thermosol dyeing range—used for continuously dyeing polyester and polyester/cellulosic blend fabrics.

In the HTN process, the fabric does not deplete dye from the dye pad solution; thus concentration of the dye pad solution is always constant. The dyer has only to ensure that enough of the solution is
supplied to the pad pan to maintain full coverage of the fabric. The dye must also control the pad side-center-side squeeze pressure to ensure uniform pickup of the dye solution by the fabric across its full width. Minor adjustments to accomplish this are easy to make.

The dye pad solution is maintained at ambient temperatures during the dyeing operation—heat is not deliberately applied. The term ambient temperatures refers to the temperature of the pad bath as it exists in the plant or facility under normal operating conditions. Operational temperatures can vary widely depending on seasonal changes and other procedures conducted in the same facility. Temperatures as high as 35°C (95°F) are typical. Temperatures above 35°C can cause the fabric to begin depleting the dye from the dye pad solution, giving rise to frontend tailing and other shading problems.

**Composition of Pad Solution**

The dye pad solution used in the HTN process is composed of 8 to 10 parts leveling agent (Product TH), 1 to 2 parts thickener and 60 to 90 parts water (all parts are listed by weight). Flame retardants, UV absorbers, antistatic agents, water repellents and other finishing and processing aids can also be formulated in the solution. A tinctorial amount of at least one acid dye is also included.

**Product TH**

Product TH is composed of a number of polyethylene glycol (PEG) derivatives. Some 50 or more PEG derivatives were evaluated before arriving at its composition. Six of the derivatives were evaluated more extensively—polyoxyethylene alkylamines, polyoxyethylene alkyl ethers, phosphoric acid alkyl ethers, polyoxyethylene acetylene ethers, boric acid alkyl esters and sorbitan alkyl esters.

Evaluation of potential ingredients included:

- **Effect on the fixation rates of the acid dyes**
- **Maximum color yield coupled with good economy**
- **Correlation between average degree of polymerization of the polyethylene alkyl ether (n) and the starting temperature of vaporization** (shown in Fig. 1).
- **Solubility of the acid dye in Product TH and its color value on the high tenacity polyamide fiber**

The most important factors in determining Product TH’s composition were dyeing results with the expected shade uniformity and strength and good fastness properties.

**Thickener SM**

Thickener SM is a balanced mixture of natural and etherified locust bean gums, carboxymethyl cellulose and polyacrylic acid type polymers. It forms a stable and homogeneous dye pad solution with all other adjuvants used in the process. It is easily washed off the dyed goods after dry heat-curing.

**Dye**

Any acid dye which is soluble in Product TH and capable of penetrating inside the high tenacity polyamide fiber and developing its true color value when dry heat is applied can be used in the HTN process.

A substantial number of acid and premetalized acid dyes were evaluated in this work. Some of the acid dyes which can be used are listed in Table I.

**Polyamide Substrate**

The polycarbonamide fiber for which the HTN process is particularly well suited can be in any structural form: i.e., light, medium and heavy weight woven and knitted fabrics of different structures constructed from flat or texturized bulked continuous filament and spun yarns of different types and counts, nonwoven, felt and carpet materials.

Polycarbonamide fibers are high modulus, high tenacity, low shrinkage polyamides made by the intermolecular condensation of linear diamines containing 6 to 10 carbon atoms with the linear dicarboxylic acids containing 2 to 10 carbon atoms. Preferably, the yarn is spun from poly(hexamethylene adipamide) or nylon 6.6, which has a draw ratio of at least 4.0 and preferably in the range of 4.6 to 5.1 (2). To give the Cordura yarn a degree of bulk equal to or greater than that in spun yarns, the filaments are texturized and bulked to become disarranged, looped and tangled within the bundle. This results in yarns of greater strength and abrasion resistance than conventional spun yarns of either cotton or man-made fibers.

Cordura nylon differs from conventional nylon in that it contains approximately twice as many amino end groups. Ballistic nylon and other high tenacity nylon products do not contain as many amino end groups as Cordura nylon but can also be dyed using the HTN process. The main difference between generic nylon 6.6 and the high tenacity nylon is the degree of structural order. Some of the properties of high tenacity Cordura nylon are compared with those of conventional nylon 6.6 in Table II.

**Dyeing and Fixation Mechanism**

The mechanism of fixation of the acid dye in the polyamide fiber is a function of its homomolecularization, caused by the action of Product TH as a fiber swelling and dye solubilizing agent. This permits diffusion of the acid dye molecules into the fiber, followed by reaction between the sulfonic group(s) of the acid dye and the amino end groups of the polyamide fiber forming ionic bonds in situ.

The use of Product TH is indispensable to this process. Optimum dye penetration and fixation is achieved while the vaporization temperature of the PEG derivatives used in Product TH is high enough to be useful in normal dry heat curing or

### Table I. Acid Dyes Which Can Be Used in the HTN Process

<table>
<thead>
<tr>
<th>Dye</th>
<th>C.I. Name</th>
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<tbody>
<tr>
<td>Nylique Yellow A-2GA</td>
<td>Acid Yellow 49</td>
</tr>
<tr>
<td>Telon Red GRL</td>
<td>Acid Red 392</td>
</tr>
<tr>
<td>Telon Fast Rubin A-5BLW</td>
<td>Acid Red 229</td>
</tr>
<tr>
<td>Telon Red FL</td>
<td>Acid Red 337</td>
</tr>
<tr>
<td>Telon Fast Red AFG</td>
<td>Acid Red 360</td>
</tr>
<tr>
<td>Nylique Red A-2B</td>
<td>Acid Red 286</td>
</tr>
<tr>
<td>Nylique Red AB</td>
<td>Acid Red 396</td>
</tr>
<tr>
<td>Telon Blue BL</td>
<td>Acid Blue 72</td>
</tr>
<tr>
<td>Ernonyl Blue 7G200</td>
<td>Acid Blue 239</td>
</tr>
<tr>
<td>Nylique Green C-3G</td>
<td>Acid Green 28</td>
</tr>
<tr>
<td>Nylique Green C-2G</td>
<td>Acid Green 25</td>
</tr>
</tbody>
</table>

* Chemical structures are shown by Constitution Number in the third edition (1971) of the Colour index.

### Table II. Comparison of Conventional Nylon 6,6 with Cordura Nylon

<table>
<thead>
<tr>
<th>Property</th>
<th>Conventional Nylon 6,6</th>
<th>High Tenacity Cordura Nylon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amino End Groups (meq/kg)*</td>
<td>35 to 40</td>
<td>75 to 80</td>
</tr>
<tr>
<td>Crystalline Orientation (relative units)</td>
<td>100</td>
<td>200 to 400</td>
</tr>
<tr>
<td>Draw Ratio</td>
<td>3 to 4</td>
<td>4 to 5</td>
</tr>
<tr>
<td>Top</td>
<td>5 to 1</td>
<td>Higher</td>
</tr>
<tr>
<td>Breaking Tenacity (g/denier)</td>
<td>2.5 to 5.0</td>
<td>5.9 to 9.8</td>
</tr>
<tr>
<td>Wet</td>
<td>2.0 to 5.5</td>
<td>5.1 to 8.0</td>
</tr>
<tr>
<td>Ultimate Elongation (%)</td>
<td>25 to 65</td>
<td>15 to 28</td>
</tr>
<tr>
<td>Dry</td>
<td>30 to 70</td>
<td>18 to 32</td>
</tr>
<tr>
<td>Wet</td>
<td>88</td>
<td>89</td>
</tr>
</tbody>
</table>

thermosol operations. As a consequence, Product TH loss is minimized and dye color yield is maximized.

To achieve good dyeings in terms of shade, strength of color and fastness properties, proper dye selection is essential as well as the use of an optimized quantity of Product TH in the dye pad solution.

The following examples demonstrate the HTN Process. All parts and percentages noted are by weight unless otherwise indicated.

**Example 1**
A plain weave nylon fabric made of 1000/140 Bright T-440 Du Pont Cordura nylon 2X warp yarn and 1000/140 Bright T-440 Du Pont Cordura nylon filling yarn weighing 97.6 pounds per 100 cloth yards was padded and evenly squeezed in open width form to about 80% pickup under ambient temperatures in a cold (unheated) 27°C (80°F) dye pad solution having the following composition:

- 30 parts Nylomine Yellow A-2GA
- 165 parts Thickener SM (7% aqueous solution)
- 90 parts Product TH
- 715 parts water

for a total of 1000 parts. The fabric was then dried at 149°C (300°F) for two minutes, and consequently heat cured in an oven for two minutes at 215°C (420°F) under atmospheric pressure. The cured fabric was then rinsed in cold and hot water, scoured in an aqueous solution containing 0.5% sodium carbonate and 0.2% of a nonionic detergent at 80°C (176°F), rinsed in hot and cold water and dried. A yellow fabric was produced having good overall fastness properties and complete dye penetration inside the fiber.

**Example 2**
The procedures of Example 1 were repeated using the following dyes in the dye pad solution:

- 11.5 parts Nylomine Blue AG (C.I. Acid Blue 25)
- 16.8 parts Nylomine Yellow A-2GA (C.I. Acid Yellow 49)
- 1.2 parts Telon Red GRL (C.I. Acid Red 392)

A uniformly dyed olive green fabric was produced with good overall fastness properties and complete dye penetration inside the fiber.

**Conclusion**
The HTN Process for the coloration of fabrics constructed from high modulus, high tenacity, low shrinkage polyamide flat and texturized filament yarns is efficient and economical in producing first quality dyed goods with excellent overall colorfastness to light, washing and crocking without adversely affecting tensile and physical properties. A substantial number of acid dyes can be used in this process, enabling the dyer to dye goods in any color required.

Contrary to other methods, developing the full shades of acid dyes does not require the use of atmospheric or pressurized steamers. Existing dyeing equipment, such as a thermosol range used in the continuous dyeing of polyester and polyester/cellulosic blend fabrics, can be used in the HTN process, with similar dyeing procedures and techniques, thereby allowing the full utilization of equipment and operators.

A variety of other types of goods constructed from regular nylon 6,6, nylon 6, wool and silk can also be continuously dyed with acid dyes using the HTN Process. The use of the process on these other substrates is being evaluated.

**References**


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