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POLYAMIDES CONTAINING BUTYROLACTONE

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PERCENT BUTYROLACTONE ADDED TO POLY (EPSILON CAPROLACTAM) CHIPS

END GROUPS (MIEQUivalents per 113 grams of polymer)

CARBOXYL END GROUP

AMINE END GROUP

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POLYAMIDES CONTAINING BUTYROLACTONE

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This invention relates generally to modified synthetic linear polyamides and more particularly to the production of poly(episolon-caprolactam) which has been modified to decrease its dyeability and improve the light stability. It is well known to treat polyamides with various agents in order to increase their affinity for certain dyes. This is a relatively common practice with such polyamides as polyhexamethyleneadipamidim (nylon 66) because of its inherent low order of dyeability. The reaction is usually one in which the polymer chain is substituted with additional reactive groups or shortened to give end groups, thereby providing an increased number of dye sites and resultant increase in dyeability with respect to various acid dyes. However, in the case of polyamides such as poly(episolon-caprolactam) (nylon 6), which possesses a larger number of available dye sites in relation to polyhexamethyleneadipamidim and thus is easier to dye, it is sometimes desirable to decrease the dyeability of the polymer. For example, a poly(episolon-caprolactam) yarn of decreased dyeability can be combined with normal poly(episolon-caprolactam) yarn in carpets and fabrics. When dyed, a two-tone effect results due to the variance in dyeability between the treated and untreated polyamides. This effect is sometimes accomplished by using certain dye-resists such as the soluble sulfur-phenol condensates which are applied directly to the finished fibers or yarn prior to weaving or tufting. However, the use of dye-resists with poly(episolon-caprolactam) yarn is unsatisfactory because they often impair the light fastness of the finished product. Fabrics treated in this manner tend to fade quickly when exposed to ultraviolet light and are therefore undesirable in a number of end uses. Moreover, certain dye-resists produce a decrease in the light stability of the yarn itself thereby diminishing the strength of the yarn upon exposure to sunlight.

It is therefore an object of this invention to provide lighter-dyeing synthetic linear polyamid fibers and yarns not having the aforementioned disadvantages.

Another object of this invention is to provide a process for decreasing the dyeability and improving the light stability of poly(episolon-caprolactam). Still another object of this invention is to provide a modified fiber-forming poly(episolon-caprolactam) that will resist the action of conventional acid dyestuffs to a limited degree and when dyed will not fade when exposed to sunlight.

A further object of this invention is to provide a modified fiber-forming poly(episolon-caprolactam) possessing decreased dyeability properties and an improved resistance to light degradation.

These and other objects will become apparent from the following detailed description.

In accordance with this invention, it has been discovered that a synthetic linear polyamide such as poly(episolon-caprolactam) can be modified to possess decreased dyeability properties by incorporating into the polymer melt prior to fiber formation a small amount of butyrolactone. Not only does the product have reduced dyeability properties but it also possesses a greater resistance to degradation from ultraviolet light and when dyed is lightfast. The process is applicable generally to all synthetic linear polyamides having NH₂ end groups. It is particularly desirable for use with those polyamides having a greater affinity for dyes such as poly(episolon-caprolactam). Without intending to be bound thereby, it is believed that the butyrolactone reacts with the amino end groups in the polymer and thus reduces a portion of the said dye sites normally present therein. The modified polymer will then have hydroxyl end groups in place of the amino end groups. Alternately, water may split out resulting in cyclic end groups. In either case, the amino group is effectively blocked from reaction with acid dyes. While the modified polyamide may be dyed with any of the conventional dyes used in dyeing nylon 6 and nylon 66, only the acid dyes and premetalized acid dyes produced the desired lighter dyeing results since the effective dyeing of each is reduced due to the reduction in amino groups or dye sites in the polymer chain.

The amount of butyrolactone added to the fiber-forming synthetic linear polyamide can be varied, depending on the results desired. Amounts less than 0.2% by weight butyrolactone based on the weight of the polyamide are in general too little to cause any appreciable blocking of dye sites and attendant decrease in dyeability in the polymer. While there is no upper limit to the amount of butyrolactone which can be added, it has been found that amounts above 3% cause considerable difficulties in spinning and processing of the polymer prior to fiber or filament formation. Preferably, amounts of butyrolactone ranging from 1% to 2% by weight based on the weight of the polyamide are employed in the process.

The figure shows graphically the relationship between the butyrolactone concentration in the polymer based on the amount added to the chips and the amino end groups and carbonyl end groups present in the polymer.

The butyrolactones may be incorporated into the preformed polymer in a number of ways. For example, it may be added directly to the polymer melt in any stage of the process prior to extrusion. In one method, it is added to granules or chips of the polymer prior to melt formation and thoroughly tumbled therewith to effect adequate mixing. In the preferred practice of the invention, the process comprises adding butyrolactone to the poly(episolon-caprolactam) chips immediately after they have been tumble-dried to remove excess moisture and thus are still hot, i.e. a temperature of 90-95°C. Addition of the butyrolactone to the hot chips results in better absorption and more freely flowing chips which aids in chip transportation during subsequent operations. If the addition takes place before the chips are dried, substantial loss of butyrolactone is experienced due to evaporation in the dryers. Following addition, the chips and butyrolactones are thoroughly tumbled or otherwise mixed to produce a uniform mixture of chips and butyrolactone prior to melt formation. Thereafter, the chips are passed to a conventional melting device and extruded or spun at a temperature ranging from 265°C. to 280°C.

Conventional melting and spinning procedures and equipment customarily used in the production of polyamide fibers may be used with the butyrolactone modified polymer and the fiber product may be drawn and processed into yarn by any known means.
poly(epsilon-caprolactam) yarn product can then be woven with normal poly(epsilon-caprolactam) yarn into fabrics or tufted into carpets, and when dyed with a single acid dye using standard procedures a striking two-tone effect is produced in the finished product. Further dyeing with disperse dyes can produce a two-color product.

For purposes of illustration, the following examples are given. However, the invention is not intended to be limited thereby.

Example I

Fiber-forming poly(epsilon-caprolactam) chips, prepared by conventionally polymerizing epsilon-caprolactam and extruding and chopping the polymer into chips, were dried at 90-95°C. in a tumble dryer to remove moisture. Immediately following drying and while the chips were in the dryer and still hot, 2% by weight butyrolactone was sprinkled over the chips and thoroughly mixed therewith by tumbling in the dryer. The thus-treated chips were conventionally melt spun and processed to give a 1090 denier, 83 filament yarn. A control yarn sample was also prepared using the same equipment, spinning, and processing conditions except that the butyrolactone addition was eliminated. Both yarns were tufted into a carpet in alternating rows of modified yarn with control yarn. Several samples of this carpet were then conventionally dyed with different acid dyes. One of the dyes used was C.I. Blue Acid 92, a monoazo dye, the chemical constitution of which is designated by Colour Index No. 13,390. In each case the modified poly(epsilon-caprolactam) yarn dyed considerably lighter than the control yarn producing a striking contrast in the carpet.

An identical group of carpet samples were similarly dyed with acid premetallized dyes. The modified yarn showed a lower degree of dyeability than the control yarn in each sample resulting in an excellent contrast in the carpet. The carpet samples dyed with both the acid dyes and premetallized acid dyes showed excellent light fastness when exposed to direct sunlight in both the modified yarn and normal yarn sections.

Example II

Polyamide chips prepared in the same manner as those of Example I were treated with 1% by weight butyrolactone in a tumble dryer immediately following completion of the drying operation and while the chips were still hot. Thorough mixing was effected by further tumbling and the polymer was conventionally melt spun and processed into 1090 denier, 83 filament yarn. Untreated control yarn prepared identically except that the butyrolactone addition was eliminated was tufted into carpets in alternating rows with the butyrolactone modified yarn. A series of samples of this carpet was conventionally dyed with the same acid dyes and premetallized dyes used in Example I. Good contrast resulted in each sample between the modified yarn and control yarn.

Example III

An undyed carpet sample prepared in the manner described in Example I was immersed for 60 minutes in a boiling dyebath maintained at pH 8-9 and which contained 0.4% of an acid premetallized yellow dye and 1.39% of C.I. Disperse Blue 3, an anthraquinone dye designated by Colour Index No. 61505. The resulting carpet was a contrasting blue/green showing that the modified yarn picked up much less of the acid dyestuff producing an overall blue color from the disperse dye whereas the untreated control accepted greater amounts of the yellow acid dye such the end result was a green due to the combined effect of the acid yellow and disperse blue dyes.

Example IV

A series of weatherometer tests were run to show the improved light stability of butyrolactone modified poly(epsilon-caprolactam) over untreated poly(epsilon-caprolactam). A twin carbon arc Atlas Weather-Ometer that had been modified to give a more severe exposure was used for the tests. The samples were exposed at 190°F to the light for 228 minutes and then to vapor from a shielded water spray for 60 minutes. The data is set forth in the table below for 200 denier, 32 filament yarn prepared in the same manner as that described in Example I.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Original Properties</th>
<th>80-hour Weatherometer (Test Data)</th>
<th>120-hour Weatherometer (Test Data)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Percent Butyrolactone</td>
<td>Tenuity (g.p.d.)</td>
<td>Elongation Percent</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>4.32</td>
<td>38.3</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>4.68</td>
<td>32.1</td>
</tr>
<tr>
<td>3</td>
<td>0.75</td>
<td>4.46</td>
<td>35.4</td>
</tr>
<tr>
<td>4</td>
<td>1.9</td>
<td>4.39</td>
<td>22.0</td>
</tr>
<tr>
<td>5</td>
<td>1.5</td>
<td>4.34</td>
<td>27.2</td>
</tr>
<tr>
<td>6</td>
<td>1.5</td>
<td>4.30</td>
<td>36.0</td>
</tr>
<tr>
<td>7</td>
<td>1.5</td>
<td>4.39</td>
<td>25.0</td>
</tr>
<tr>
<td>8</td>
<td>1.5</td>
<td>4.42</td>
<td>26.3</td>
</tr>
</tbody>
</table>

The above data clearly shows that the modified polymer has much improved light stability properties over the control polymer when treated under identical conditions.

While the invention has been described with particularity in connection with poly(epsilon-caprolactam), it is applicable generally to numerous other polymers to produce a decrease in dyeability and still retain light fastness when dyed. The invention is therefore intended to be limited only to the extent set forth in the following claims.

What is claimed is:

1. A process for decreasing the dyeability of fiber-forming polyamides comprising dispersing in a melt of a preformed polyamide at least 0.2% by weight of butyrolactone based on the weight of the polyamide.

2. The process of claim 1 in which the polyamide is poly(epsilon-caprolactam).

3. The process of claim 1 in which from 1.0% to 2.0% butyrolactone is dispersed in the polyamide melt.

4. A process for producing lighter dyeing poly(epsilon-caprolactam) fibers and filaments having an improved light stability comprising mixing butyrolactone with granules of a preformed poly(epsilon-caprolactam) polymer in amounts of at least 0.2% by weight of the polymer, and thereafter melting the mixture and extruding it into fibers and filaments.

5. The process of claim 4 in which from 1.0% to 2.0% butyrolactone are mixed with said polymer.

6. A process for decreasing the dyeability and improving the light stability of poly(epsilon-caprolactam)
fibers and filaments comprising mixing butyrolactone with hot granules of a preformed poly(epsilon-caprolactum) polymer in amounts of at least 0.2% by weight based on the weight of the polymer, and thereafter melting the mixture and extruding it into fibers and filaments.

7. The process of claim 6 in which the butyrolactone is added to the hot granules after they have been dried to remove excess moisture, said granules being at a temperature ranging from 90-95°C.