Cationized Cotton: Opportunities and Challenges

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What is Cationized Cotton and Why Is It needed?

• Cotton chemically modified with permanent cationic charges
  • Cationic dye sites to attract anionic dyes
• Dyeing cotton (especially with fiber reactive dyes)
  • Salt needed (efficient exhaustion)
  • Large amounts of water and energy required (afterwash)
  • Color in effluent (hydrolyzed dye)
Cationization Methods

- Cationic Polymers
  - Ring dyeing and poor lightfastness

- Cationic Reagents
  - Uniform dyeing with minimal effect on lightfastness
  - 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC) promising approach

\[
\text{CHICH}_2\text{CHCH}_2\text{N(CH}_3\text{)}_3^+ \quad \text{Cl}^- \\
\text{CHPTAC}
\]
CHPTAC Reactions

• Synthesis

\[
\text{H}_2\text{C} \rightarrow \text{CHCH}_2\text{Cl} + \text{HN(CH}_3\text{)}_3 \xrightarrow{\text{H}} \text{ClCH}_2\text{CHCH}_2\text{N(CH}_3\text{)}_3
\]

CHPTAC

• Reactive Intermediate

\[
\text{ClCH}_2\text{CHCH}_2\text{N(CH}_3\text{)}_3 \xrightarrow{\text{NaOH}} \text{H}_2\text{C} \rightarrow \text{CHCH}_2\text{N(CH}_3\text{)}_3
\]

EPTAC
CHPTAC Reactions

- Cotton Cationization

\[
\begin{align*}
H_2C\text{-CHCH}_2\text{N(CH}_3)_3 + \text{CellOH} &\rightarrow \text{CellOCH}_2\text{CHCH}_2\text{N(CH}_3)_3 \\
\text{EPTAC} &\rightarrow \text{Cationized Cotton}
\end{align*}
\]

- EPTAC Hydrolysis

\[
\begin{align*}
H_2C\text{-CHCH}_2\text{N(CH}_3)_3 &\rightarrow \text{HOCH}_2\text{CHCH}_2\text{N(CH}_3)_3 \\
\text{EPTAC} &\rightarrow \text{Diol}
\end{align*}
\]
Application of CHPTAC

- Cold pad batch most efficient
  - CHPTAC available as 65% active solution
  - Pad 5 – 10% CHPTAC owf with ~ 2 moles of NaOH/mole CHPTAC
  - Batch 16 – 24 hours, rinse and neutralize
  - ~50% yield (higher with mercerized cotton)

- Cationizing during preparation is preferred
Dyeing Cationized Cotton

• Modified conventional procedures
  • Follow recommendations for alkali, time, and temperature
  • Remove salt
  • Reduce afterwashing
Benefits of Dyeing Cationized Cotton

- Reduced water, energy, and time
- Higher color yields

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Water Usage (L/kg)</th>
<th>Energy Usage (MJ/kg)</th>
<th>Process Time (min)</th>
<th>% Dye Exhaustion</th>
<th>K/S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cotton</td>
<td>130</td>
<td>45.9</td>
<td>230</td>
<td>87.5</td>
<td>23.8</td>
</tr>
<tr>
<td>Cationized Cotton</td>
<td>23</td>
<td>18.9</td>
<td>105</td>
<td>99.1</td>
<td>26.2</td>
</tr>
</tbody>
</table>

Fiber reactive Blue 225 (5% CHPTAC owf, 3% dye owf, 10:1 LR)
Benefits of Dyeing Cationized Cotton

- More efficient use of dye

0.61% dye  0.41% dye
Benefits of Dyeing Cationized Cotton

- Lower total cost
  - Pilot plant dyeing comparisons
    - 55 pound tubular knit dye lots
    - 4.3% owf CHPTAC application
    - 33% less dye at matched shades
    - 19% overall cost savings
What Could Possibly Go Wrong?

• Rapid dye strike → unlevel dyeings
• Conventional dye formulas give different shades → shades rematched
• More dye sites than dye → dye pickup during laundering
Improving Dye Levelness

• Anionic leveling agents

\[
\text{dye}^- \quad \text{dye}^- \quad \text{dye}^-
\]

• Carboxymethyl cellulose effective

\[
\text{OCH}_2\text{C} - \text{O}^-
\]
Improving Dye Levelness

1% Reactive Red 239

1% Reactive Red 239

No Leveling agent
1% Chromabond S-100
5% Chromabond S-100
10% Chromabond S-100

Dyeing time, min

% Exhaustion
Improving Dye Levelness

1% Reactive Red 239
Effect of Dye Structures on Adsorption and Exhaustion Rates

- Five dyes with different structures
  - Molecular weights
  - Number of anionic groups

<table>
<thead>
<tr>
<th></th>
<th>Reactive Blue 19</th>
<th>Reactive Violet 5</th>
<th>Reactive Red 11</th>
<th>Reactive Red 198</th>
<th>Reactive Blue 109</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW g/mole</td>
<td>627</td>
<td>736</td>
<td>767</td>
<td>968</td>
<td>1040</td>
</tr>
<tr>
<td># SO$_3^-$ *</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>4</td>
<td>5</td>
</tr>
</tbody>
</table>

* includes SO$_3^-$ from sulfatoethyl sulfone groups
Reactive Red 11

Reactive Red 198

NC STATE
Equilibrium Adsorption Results

Reactive Blue 109 at 40 °C
Equilibrium Adsorption Results

10% owf CHPTAC at 40 °C
Dye Exhaustion

• Mathis JFL dyeing machine with HueMetrix monitoring system

  • Dye concentrations adjusted to give equimolar dyeings
  • No salt with cationized dyeings
  • Recommended alkali amounts
Dye Exhaustion Results

<table>
<thead>
<tr>
<th></th>
<th>% Exhaustion</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cotton Fabric</strong></td>
<td></td>
</tr>
<tr>
<td>Reactive Blue 19</td>
<td>1.81 % owf</td>
</tr>
<tr>
<td>Reactive Violet 5</td>
<td>2.12 % owf</td>
</tr>
<tr>
<td>Reactive Red 11</td>
<td>2.21 % owf</td>
</tr>
<tr>
<td>Reactive Red 198</td>
<td>2.79 % owf</td>
</tr>
<tr>
<td>Reactive Blue 109</td>
<td>3.00 % owf</td>
</tr>
<tr>
<td>627 g/mole</td>
<td>736 g/mole</td>
</tr>
<tr>
<td>767 g/mole</td>
<td>968 g/mole</td>
</tr>
<tr>
<td>1040 g/mole</td>
<td></td>
</tr>
<tr>
<td><strong>Untreated Cotton</strong></td>
<td>82.6</td>
</tr>
<tr>
<td></td>
<td>69.6</td>
</tr>
<tr>
<td></td>
<td>70.4</td>
</tr>
<tr>
<td></td>
<td>65.9</td>
</tr>
<tr>
<td></td>
<td>61.2</td>
</tr>
<tr>
<td><strong>2.5 % owf CHPTAC</strong></td>
<td>66.2</td>
</tr>
<tr>
<td>Cotton</td>
<td>59.0</td>
</tr>
<tr>
<td></td>
<td>61.3</td>
</tr>
<tr>
<td></td>
<td>53.2</td>
</tr>
<tr>
<td></td>
<td>50.3</td>
</tr>
<tr>
<td><strong>5.0 % owf CHPTAC</strong></td>
<td>90.8</td>
</tr>
<tr>
<td>Cotton</td>
<td>81.7</td>
</tr>
<tr>
<td></td>
<td>83.2</td>
</tr>
<tr>
<td></td>
<td>70.4</td>
</tr>
<tr>
<td></td>
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</tr>
<tr>
<td><strong>10.0 % owf CHPTAC</strong></td>
<td>98.1</td>
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<tr>
<td>Cotton</td>
<td>94.2</td>
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<td></td>
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<td></td>
<td>89.6</td>
</tr>
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<td></td>
<td>85.2</td>
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</table>
Color Matching with Cationized Cotton

• Existing color primaries give poor matches on cationized cotton

• Color primaries developed with cationized cotton provide closer matches on cationized cotton
# Color Matching with Cationized Cotton

<table>
<thead>
<tr>
<th></th>
<th>Shade One</th>
<th>Shade Two</th>
<th>Shade Three</th>
</tr>
</thead>
<tbody>
<tr>
<td>% dye</td>
<td>0.324</td>
<td>0.315</td>
<td>0.814</td>
</tr>
<tr>
<td>ΔEcmc</td>
<td>4.22</td>
<td>1.20</td>
<td>2.06</td>
</tr>
</tbody>
</table>
Capping Excess Dye Sites

- Dye transfer during AATCC TM 61-2A

untreated cotton

fiber reactive dyed w/o afterwash

7.5% CHPTAC cationized cotton
Capping Excess Dye Sites

- Sera Fast N-HF-01 (high molecular sulfonic acid)

![uncapped cationized cotton](image)

![capped cationized cotton](image)

uncapped cationized cotton

capped cationized cotton

2g/L 15 minutes at 60 °C
Printing Cationized Cotton

• Screen printing of pigments
  • Improved wash fastness
• Screen printing of direct dyes
  • Excellent wash fastness
• Inkjet printing of fiber reactive dyes
  • Increased color yield and outline sharpness
  • Reduced steaming and wash off time
• Concerns with white ground staining
Commercially Viable Cationized Cotton

- Lower cost approach to more sustainable cotton dyeing
- Leveling concerns
  - Leveling agents available
  - Match dye sites and dye concentrations
- Color matching
  - New color primaries
  - Select dyes with similar exhaustion rates
- Color transfer
  - Capping agents available
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