AATCC Symposium
Shining a Light on Flammability in Textile Application

Insights and Perspectives to the Dyeing of Engineered Flame Resistant Fibers and Fabrics

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Agenda

1. Overview of Wet Processing
2. Typical Dyeing Equipment
3. Why Insights and Perspectives?
4. Aramids
5. Modacrylic and Variants
6. Polyester
7. Rayon
8. Last Shot!
Overview of Wet Processing

**Preparation**
- process to remove extractables
  - fiber finish, oils, waxes, sizes, etc.
- may be aqueous batch or continuous for knits and wovens
- stabilize fabric for shrinkage or rope marks – usually aqueous and dry heat

**Objective:** uniformly clean the fiber or fabric for successful dye and finish application.
Fundamentals of the Process

**Preparation**

**Dyeing**
- process depends on the fiber or fiber blend, dye class, and type of substrate (yarn or fabric)

**Finishing**

**Objective**: uniform application of color to achieve shade and color fastness properties.
Type Dyeing Equipment – Knit, Woven, Yarn

(Courtesy various sources)
Fundamentals of the Process

Preparation

Dyeing

Finishing

**Finishing**
- achieve the **final physical properties** (shrinkage, width, etc.)
- apply the **functional properties** (softness, repellence/release, moisture management/comfort, fire protection, etc.).
- develop **surface effect** (suede, brush, sand)

**Objective:** uniformity, achieve performance, and maintain shade and colorfastness.
Why Insights and Perspectives?

This market is one of:

- **high value finished product ($)**
- **high performance requirements** for different end-uses (flammability tests, colorfastness, etc.) ($)
- **requires continuous development** for new, improved, better products ($)
- **very competitive** (among the few)
Why Insights and Perspectives?

All the players (fiber, wet processor, brand or merchandiser, dye and chemical suppliers) want to:

**PROTECT INTELLECTUAL PROPERTY**
Fiber Identity:  Aramids

Chemistry:  A manufactured fiber in which the fiber forming substance is a long-chain synthetic polyamide in which at least 85% of the amide (-CO-NH-) linkages are attached directly between two aromatic rings. (FTC)

Types:  meta-aramid and para-aramid

Markets:
Fire protective apparel fabrics, filtration, insulation, transportation, electrical, ballistic
Fiber Identity: Aramids
Meta-Aramid Type Structure

Formaldehyde, CONH
CONH

NOMEX® meta-aramid [poly(meta-phenyleneisophthalamide)]

Fiber Structure has some flexibility.
Natural, off-white color.
Fiber Identity: Aramids
Para-Aramid Type Structure

Fiber Structure is more rigid.
Fiber has a yellow/golden color.
ARAMID FIBER STRUCTURE

Challenge #1

Conventional Fiber Molecular Chain Orientation - open

Aramid Molecular Chain Orientation - structured/rigid
Dyeing Aramids

Dye class: Cationic (Basic Dyes)

- Wide dye range, but limited selection to meet most shade and colorfastness requirements

<table>
<thead>
<tr>
<th>Basic (Cationic) Cationic Dyes For Aramids</th>
<th>C.I. Basic</th>
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<tbody>
<tr>
<td>Yellow 13</td>
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<td>Yellow 21</td>
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<td>Yellow 28</td>
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<td>Red 29</td>
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<td>Blue 3</td>
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<td>Blue 41</td>
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<td>Blue 54</td>
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<td>Black - mixtures</td>
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Primary dye selection for best lightfastness, but other dyes used as needed for shade or other properties.
Dyeing Aramids

Dyebath – **Challenge #2** (Major Requirements)

**Carrier**

Typical carriers used include:
- glycol (aryl) ether
- benzyl alcohol
- acetophenone
- phthalimide
- n-methylformanilide
- mixtures

Could use **30 to 100 g/L** concentration based on type and depth of shade.

**Sodium Nitrate**

**20 to 30 g/L** typical concentrations
Dyeing Aramids
Dyebath – Challenge #2 (Major Requirement)

Typical Contents

- carrier
- sodium nitrate
- acetic acid (or citric is used)
- lubricant (nonionic)
- water conditioner (chelate/sequestrant, optional)
- foam control (non-silicone)

Do your home work to optimize!
Procedure Summary:
Typical Aramid Dye Procedure

1 - carrier/pH/other
2 - dyestuff
3 - sodium nitrate
4 - drain/wash
5 - scour
Aramid Sources:

**Meta-Aramid**
Nomex® – DuPont Performance Fibers
Aramet® – Aramid HPM, LLC
Conex® – Teijin

**Para-Aramid**
Kevlar® – DuPont Performance Fibers
Paramyd® – Aramid HPM, LLC

Hybrid (meta/para)
Technora® - Teijin

and others
Fiber Identity: Modacrylic
Fiber Name: Protex® C
Supplier: Kaneka

Chemistry: manufactured ...long chain synthetic polymer composed of less than 85% but at least 35% by weight of acrylonitrile units (FTC). Comonomers are the key!

Forms: staple; bright and semi-dull

Markets:
Home and institutional uses for draperies, upholstery, carpet, bedding; protective apparel; transportation; fake fur, hair, and toy products; sleepwear
Dye class: Cationic (Basic Dyes)

- Wide range of dyes to meet most shade and colorfastness requirements.

Dyeing Conditions:

- Very similar to that of acrylic fibers
  - cationic dye linking with an anionic dye site

- Key Processing Issue:
  - Low Fiber Saturation Value (0.9-1.2, based on denier)
    - building some deep shades may be difficult
  - Limited dyeing temperature (212-217°F/100-103°C) maximum
    - exceeding will result in shrinkage and harshness
  - Glass Transition (Tg) of 194-203°F (90-95°C)
    - temperature that fiber structure opens/dyes strike
Cationic Dyes

Modacrylic Dyeing Procedure

Dye Temp: 212-217°F
Tg: 194-203°F
9 to 23°F is critical zone

- Prescour if needed
- 1 - dyebath
- 2 - dyestuff
- 3 - washing
- 4 - softener

holding and/or slow heating
Dyeing Conditions:

- Typical Dyebath
  - acetic acid (pH 3.5-5.0)
  - sodium sulfate (optional; prefer)
  - retarder/leveler (caution)
  - nonionic lubricant
  - foam control agent (non-silicone)

- Other Useful Tools
  - Dye Saturation Values – to use the fiber saturation value
  - K (Compatibility) Values – Scale of 1 to 5 (1 fast; 2 slow) to choose compatible dye formulas
  - To increase yield on dark shades – temperature (?) and/or carrier/diffusion accelerant
Other sources of modacrylic fiber:
Kanecaron® modacrylic - Kaneka
Tairylan® modacrylic - Formosa Plastics Corporation
Modac® - Aramid HPM, LLC

PyroTex® from PyroTex Fibers GmbH
• defined as an engineered acrylic
• dyeable with acid dyes (1:1 metal complex types, pH 1-2)
• light pink natural color
• use in blends with solution dyed aramids or dye in blends with wool

and others
Fiber Identity: Polyester
Fiber Name: Inhibit® and Repreve® FR
Supplier: Unifi Manufacturing Incorporated and Unifi Textiles Suzhou Co. Ltd.

Chemistry: non-halogenated, phosphorous-based chemistry. FR chemistry is inherent and performance is present for the life of the article.

Forms: filament, staple, tow; bright and semi-dull; solution-dyed colors
Fiber Identity: Polyester
Fiber Name: Inhibit® and Repreve® FR

Markets:
Home and contract textiles including upholstery, drapery & curtains, wall covering, bedding, blinds, and bedding; apparel and transportation

Note:
Inhibit based on virgin PET.
Repreve based on recycled PET.
Offer other FR fiber variants including heavy metal-free, anti-odor and antimicrobial, UV resistance, and moisture management.
The Inhibit® and Repreve® FR names are commercial trademark names.

- Unifi does not guarantee specific performances.
- Unifi does guarantee that the FR chemistry will be above specific concentrations.
Fiber Identity: Polyester
Fiber Name: Trevira CS®
Supplier: Trevira GmbH

Chemistry: phosphorous containing comonomers built into polyester chain molecules

Forms: filament and staple, various bright and dull versions; solution-dyed colors available

Markets:
Upholstery, drapery & curtains, wall covering, bedding, blinds, bedding, apparel and transportation
Trevira CS® is a branded FR polyester.

- Fabrics sold under the Trevira CS name must receive a certification for performance.
- Can self-brand
Dyeclass: Disperse Dyes
➢ wide selection to meet most shade and colorfastness requirements

Dyeing Conditions: stable to standard polyester dyeing systems including:
➢ Dyeing up to 135C/275F
➢ Typical dyebath chemicals including:
  pH control (4 to 6)
  dyeing assistants (levelers, diffusion accelerants)
  water conditioners (chelates, sequestrants)
  lubricants
  foam control agents (avoid silicone based)
➢ Alkaline or acid reduction clearing for improved colorfastness
Typical Polyester Exhaust Dye Procedure

1 - Dyebath
2 - Dyestuff
3 - Washing
4 - Post-Treatment

°F

pH Check

0 60 120 180 240
- Dye Selection and Hue Shift – little-to-no color change
- No adverse affect on colorfastness properties such as wash, light, etc.
Fiber Identity: Viscose Rayon
Fiber Name: Lenzing FR®
Supplier: Lenzing Fibers

Chemistry: proprietary organophosphate, halogen-free chemistry with durability to post-care (washing and drycleaning)

Forms: spun; solution-dyed colors. Most often in blends with modacrylics and aramid types (solution dyed)

Markets – military, law-enforcement, fire-fighting, furniture, transportation
Dye class: Fiber Reactive, Direct Dyes, and Vat Dyes
- Wide selection to meet most shade and colorfastness requirements
- Similar to dyeing cotton – rayon will have higher affinity for dyes

Fiber Reactives – most common for general fastness.

Direct Dyes – depends on wetfastness requirements. Ideal for light/pastel shades.

Vat Dyes – prefer when chlorine and high levels of lightfastness are required. Especially in some of the industrial-type wash requirements.
Typical Fiber Reactive Exhaust Procedure

A. Dyebath
B. Electrolyte
C. Alkali
D. Washing
E. Fixative

Temperature (°F)

Time (in minutes)
Typical Direct Dye Exhaust Procedures

- **A** - Dyebath
- **B** - Dyestuff
- **C** - Electrolyte
- **D** - Overflow cold rinse
- **E** - Cold circulating rinse
- **F** - Electrolyte rinse
- **G** - Fixative
Typical Vat Dye
Exhaust Procedure

A - Dyebath
B – Dye
C – Reduction Bath
D – Cold Washing
E – Oxidation and Soap
F - Washing

°F

Time (in minutes)

0  60  120  180  240

AATCC Flammability Program
General Processing Recommendations:

**Dry Fiber Heatsetting (with other blends)**
- minimize time/temperature - 180°C/356°F for 30 sec

**Wet Process (preparation/dyeing) Conditions**
- <100°C/212°F.
- Minimize use of strong alkalis (i.e. caustic liq) at high temperatures

**Dry/Finish Temperatures**
- <160°C/320°F (suggest 100-130°C/212-266°F (avoid harshness))
- Target 8-10% residual humidity in fabric
Other Sources of FR Rayon

FR Viscose T100 - Aramid HPM, LLC

and others
Fiber Identity: Polyamide imide (PAI)
Fiber Name: Kermel®
Supplier: Kermel

Chemistry: polyamide imide (classified in the meta-aramid family)

Forms: filament and staple; yellowish/orange color. Available in solution-dyed colors.

Markets:
Heat and fire protective clothing for military, aviation, fire fighters, workwear; outwear and thermal insulation (inner layer)
Kermel has no practical dyeability. Use solution-dyed fiber.

Use is mostly in blends with:
Modacrylic  Nylon  Wool
FR Rayon  Cotton  other aramids

Wet Processing Conditions are determined by the complimentary fibers:
-Kermel is not affected by the chemicals and dyes used for processing the above fibers.
Fiber Identity: Polyetherimide (PEI)
Fiber Name: Ultem
Supplier: Sabic

Dyeability:
- Disperse dyes; similar to dyeing polyester
- Caution on carrier and dyeing temperature

Fiber Identity: Polyphenylene Sulfide (PPS)
Fiber Name: PPS
Supplier: Durafiber

Dyeability: none; natural or solution dyed
Note: When considering blends of engineered flame resistance fibers with:

- Other engineered FR fibers
- Non FR fibers and topically treating

It’s a “whole new ball game” on procedure design because of a specific fiber’s compatibility and process stability limits to temperature and chemicals of the companion fiber.
Finishing of Engineered Flame Resistant Fabrics

**Typical Topical Treatments**

- Sewing lubricants
- Repellents (water/soil)
- Moisture management
- Antimicrobial/anti-odor
- Fire retardant chemicals
- Cross-linking resins
- Other proprietary additives
With All Engineered Flame Resistant Fibers

Do your Homework:

✓ Know your fiber, source, quality
✓ Know the fiber supplier’s process recommendations
✓ Work with the chemical/dye suppliers
✓ Ensure all chemicals used in the wet processing will not contribute to flammability and test failures
✓ Ensure residuals are removed through washing or alternative steps.
✓ Don’t take for granted - do your homework and testing.
✓ Make changes carefully….."same as" is not always true!