# High Strength Carbon Fibers

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Project ID: ST093

# Overview

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## Timeline

- Start 2007
- Project End date: 2015
- 10% completed

## Barriers

- High cost of high strength carbon fibers
- Carbon fiber account for ca. 65% of the cost of the high pressure storage tanks

## Budget

- FY07 $600K
- FY08 $0
- FY09 $200K
- FY10 $200K

## Partners

- ORNL (Host side)
- Virginia Tech - VT

# Relevance



Objective: to reduce the manufacturing cost of high-strength carbon fibers by means of:

- Significant reduction in the production cost of the PAN-precursor via hot melt methodology
- Later on, the application of advance carbon fiber conversion technologies (in) development at ORNL.

*This melt-spun PAN precursor technology has the potential the reduce the production cost of the high strength carbon fibers by > 30%. The additional application of advanced conversion technologies (ORNL) could further reduce this cost by another ~20%.*

# Melt-Spun PAN Precursor - Introduction

- Currently, ALL commercial PAN precursor is wet spun
  - Pure PAN has a lower degradation temperature than melt temperature
  - Formulation to render PAN melt spinnable generally reduces the finished fiber strength
  - ORNL and its partners are exploring novel approaches to render PAN melt spinnable with minimum copolymer content
- Wet spinning is capital intensive due in part to the solvent handling and recovery systems
  - Wet spinning solvents may be highly corrosive and environmentally hazardous
  - Wet spinning plants have very high "plant holdup" and pumping requirements to move the solvent
- Wet spun fibers are more likely to have flaws or bubbles
- Very complicated/cost intensive to produce flow-free, high purity PAN filaments
- Melt spinning is a higher throughput process

# Melt-Spun PAN Precursor is partially Proven Technology



- BASF developed melt-spun PAN precursor in the 1980's
  - Carbon fibers were qualified for B2 bomber
  - Demonstrated 400 – 600* ksi fiber strength and 30 – 40 Msi modulus; even better properties were thought to be achievable
  - PAN content was 95% - 98% (consistent with high strength)

*Future HS-CF will need values around 700ksi

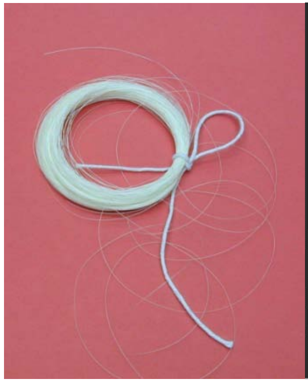
# Melt-Spun PAN Precursor (cont'd)

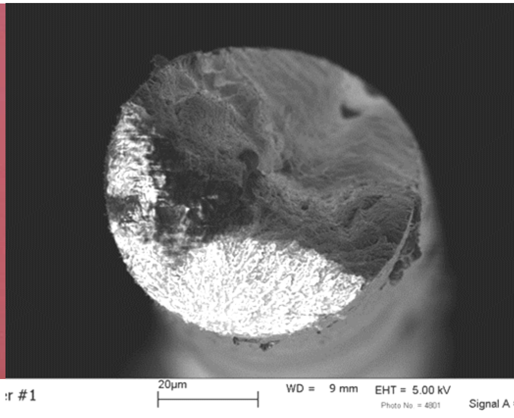


- Significantly lower production cost than wet-spun fibers
  - ~ 30% lower precursor plant capital investment
  - ~ 30% lower precursor plant operating cost
  - Typical precursor line speed increased by ≥ 4X at winders
- Program was terminated in 1991 due to carbon fiber market collapse at cold war's end, a forecasted long (~10yr) recovery period, and solvent issues (acetonitrile, nitroalkane)
- Information provided by Joe Venner of BASF
  - Co-inventor of BASF melt spinning technology
  - Key member of BASF development team
- Various US Patents and publications are available from this BASF development time.

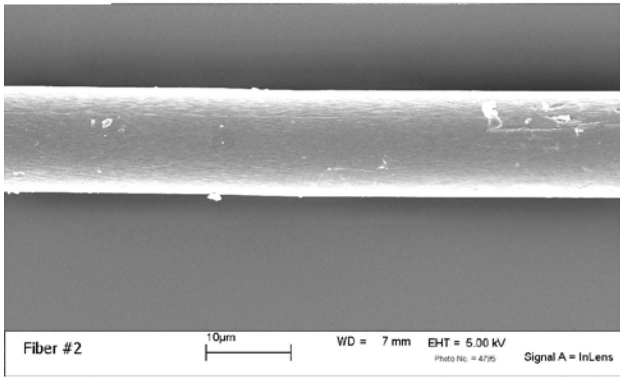
# Mechanical Accomplishment - Progress Status

- Demonstrated feasibility of using benign plasticizers to melt spin PAN and promote higher degree of drawing
- Novel comonomers were successfully incorporated
  - Initially produced: Foamed PAN fibers and high molecular weight “fibrous” materials (4/08)
- First (low-quality) fibers were melt spun (2008 to mid 2009)
- Actual, produced PAN filaments:
  - Moderate quality
  - Large diameters
  - Need increase AN contain, > 95%






- **Key technical issue: Improve melt stability by reducing Tm below the PAN degradation temperature.**



# FY10 Milestones

| Task/ Subtask | Title | Milestone/Deliverable Description | Planned Completion Date |
|---|---|---|---|
| Precursor Development | Melt stable PAN filaments | Single filaments drawn from melt stable polymer with 92 – 95 mol% AN | 12/2009 |
| | Multi-filament precursor tow | Make > 10-foot long "micro-tow" w ≥ 10 filaments, with 10 – 20 μm filament diameter and ≤ 1 vol% filament porosity | 03/2010 |
| | $2^{nd}$ generation multi-filament precursor tow | Make > 10-foot long "micro-tow" w ≥ 10 filaments, with chemistry and process modified to increase carbon fiber mechanical properties | 07/2010 |
| Conversion | 150 ksi multi-filament carbon tow | Melt spun PAN fibers converted with mean single-filament or tow tensile properties 15 Msi modulus and 150 ksi ultimate strength | 05/2010 |
| | 200 ksi multi-filament carbon tow | Melt spun PAN fibers converted with mean single-filament or tow tensile properties 18 Msi modulus and 200 ksi ultimate strength | 09/2010 |

# Leveraging

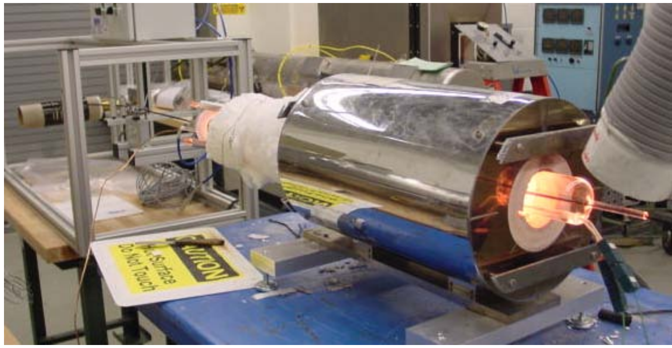


- The $H_2$ high strength carbon fiber program is a major beneficiary of a decade of prior investments in carbon fiber R&D at ORNL
  - Successful in developing revolutionary new approaches to precursor and conversion technology (Advanced Oxidation and MAP)
  - Unique physical resources specific to carbon fiber R&D
  - Access to ORNL's extensive materials processing and characterization capabilities
  - Development of extensive intellectual expertise including an established network of university and industry partners

# Unique ORNL Capability – Precursor Evaluation System



- **Designed for development of conventional processing recipes with limited quantities of precursor**
  - Residence time, temperature, atmospheric composition, and tension are independently controlled in each furnace
  - Can process single filament up to thousands of filaments
  - Precise tension control allows tensioned processing of ~20-filament tows



# Unique ORNL Capability – Conventional Pilot Line



- 1:20 scale of a commercial grade production line
- Capacity for 8 tows
- Upgrades underway for automated operation and production of high strength carbon fiber
- Unique capability among FFRDC's and universities

# Textile PAN Precursor



- **ORNL and FISIPE have conducted extensive work on commodity grade fibers from textile PAN precursor and are currently evaluating large carbon fiber tows**

- **Modified textile PAN with methyl acrylate (MA) comonomer should enable a moderate- to high-strength fiber at lower cost**

- **FISIPE is aggressively pursuing the development of a new textile PAN precursor that may be applicable for high strength carbon fibers**

# ORNL Advanced Conversion

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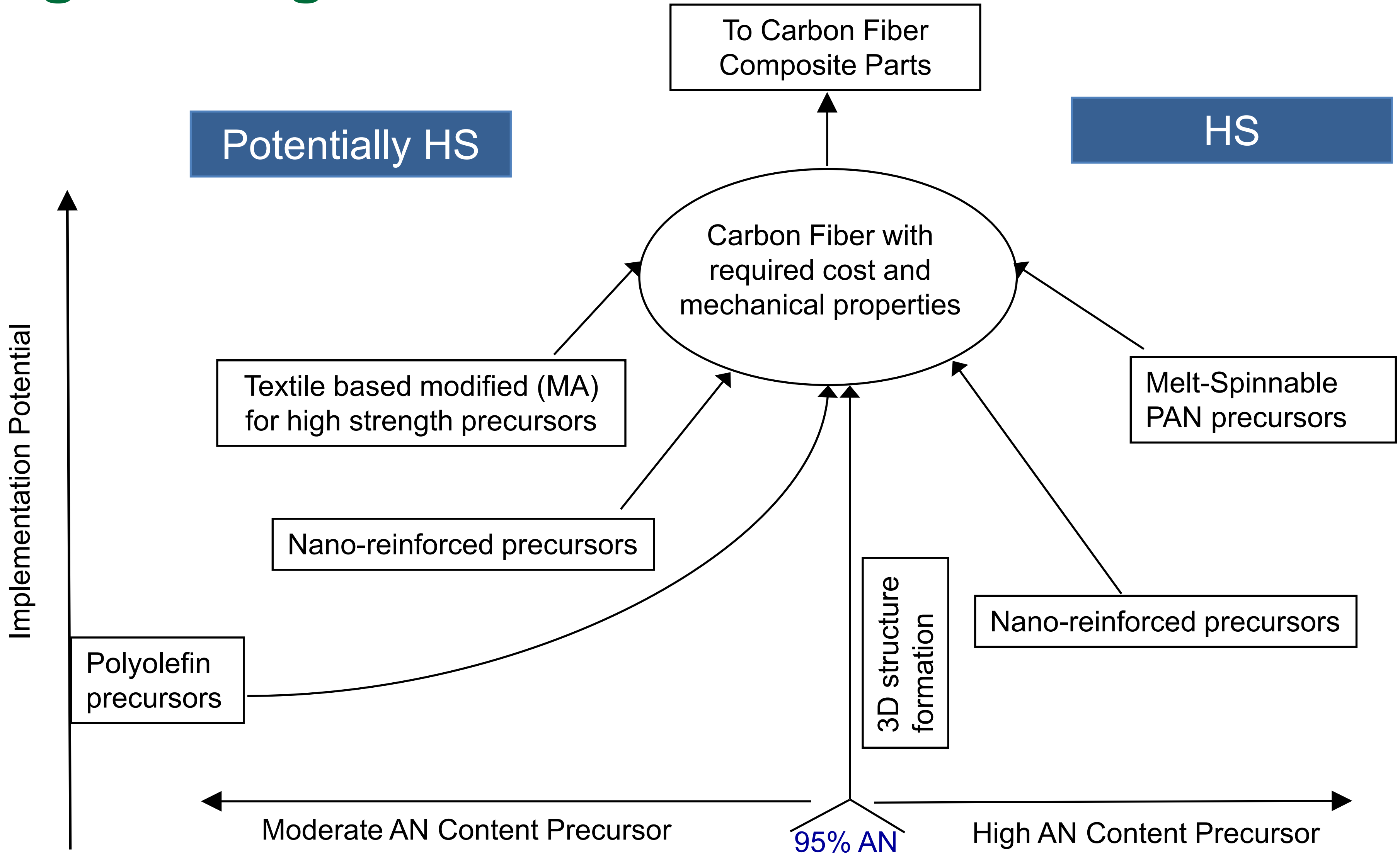
- Oxidation / Stabilization
  - Cross-links and oxidizes the fibers; conventionally requires 70 – 120 minutes, diffusion controlled process ($O_2$)
  - Principal development based on atmospheric pressure plasma
    - Demonstrated ~ 30 minute residence time, scalable.
    - Current scale is one 3k tow oxidized at 0.3 m/min
    - Process scaling to commence soon
- Microwave-assisted plasma carbonization
  - Demonstrated single large tow line speed ~ 5 m/min
  - Demonstrated 3-tow processing at > 1 m/min
  - Satisfied property targets for automotive structural applications

# High-Strength Carbon Fiber – Potential Routes



# Cost Modeling

- **Kline and Company has been cost modeling carbon fiber manufacturing for the Automotive Composites Consortium since 2003**
- **Kline has completed models on high strength carbon fibers made from wet-spun PAN (baseline) and melt-spun PAN**
- **Kline's models are fairly rigorous and moderately conservative**
- **The appropriate use of the Kline model results is for comparison and trending**
  - **select the most promising research approaches**
  - **identify critical cost sensitivities**
  - **establish scaling targets**
- ***Cost* is the manufacturer's cost to produce; *price* is highly dependent on carbon fiber market conditions**

# Estimated Precursor Cost

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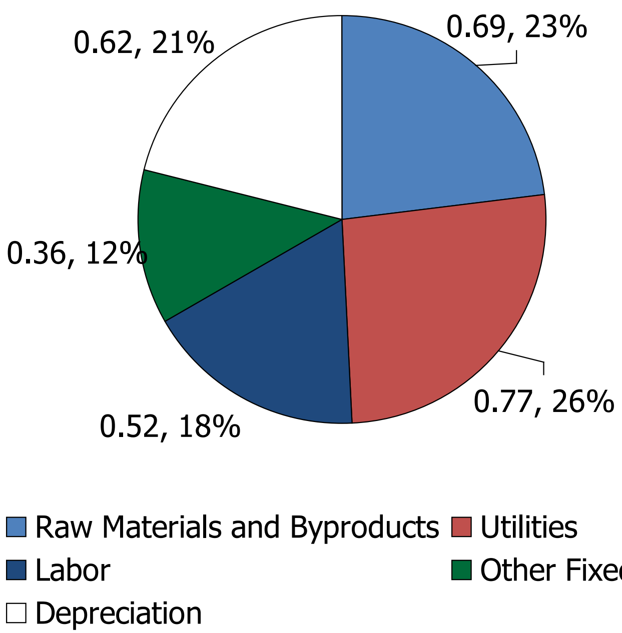
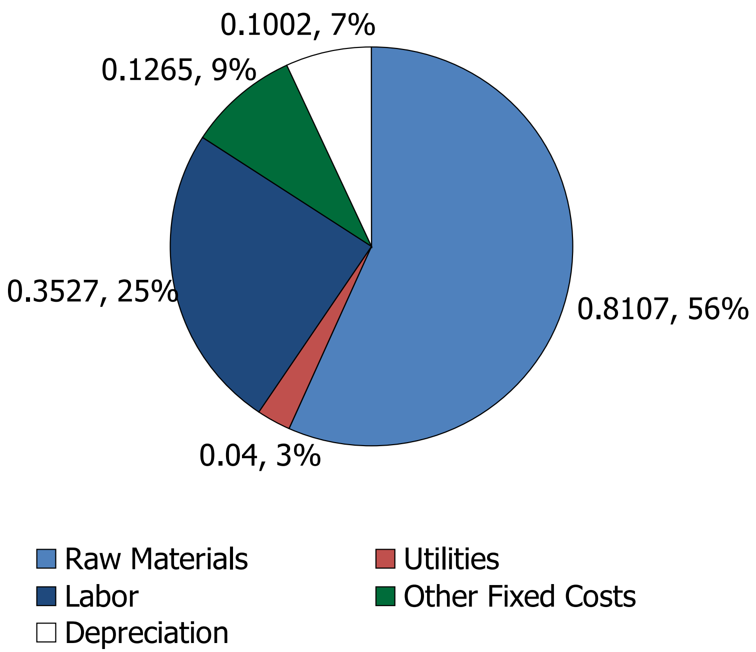
## Wet-Spun PAN Cost Structure
## $2.97/lb of Precursor




Line speed ~ 200 m/min

## 3x Melt-Spun PAN Cost Structure
## $1.43/lb of Precursor



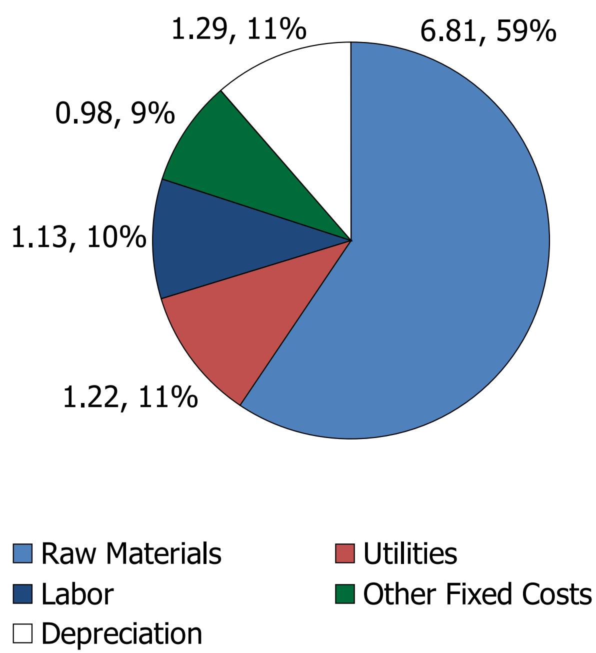

Line speed ~ 1,800 m/min

Precursor plant scale is 12M lb/yr of precursor fibers. Melt spinning rate is assumed to be 3X that of pitch.

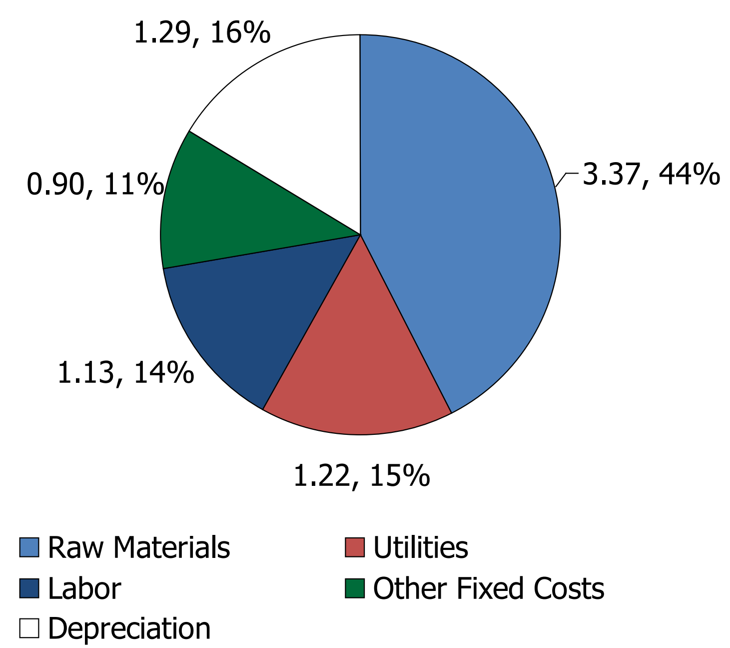
Source: Kline and Company, November 2007; estimates based on oil at $60/bbl

# Estimated Finished Carbon Fiber Cost

## Wet-Spun PAN Carbon Fiber
## $11.43/lb




## Melt-Spun PAN (3x) Carbon Fiber
## $7.91/lb




Conversion plant scale is 5M lb/yr of finished carbon fiber.

Source: Kline and Company, November 2007; estimates based on oil at $60/bbl

# Potential CF Cost Matrix



**Estimated cost based on implementation of IP from ORNL program**

| Precursor and Conversion | Mill Cost $/lb CF |
|---|---|
| *Baseline* – Wet spun PAN precursor conventionally converted | $11.43 |
| Melt spun PAN precursor conventionally converted | $ 7.91 |
| Melt spun PAN, advanced oxidation, conventional carbonization | $ 6.83 |
| Melt spun PAN, advanced conversion | $ 6.11 |

*Mill cost* is the manufacturer's to produce finished carbon fibers. These cost estimates are derived primarily from the 2007 Kline reports and are based on petrochemical prices in CY2007Q1

# Collaborations and Partnerships



- Virginia Tech
  - A leading US university in synthesis and processing of PAN-based polymers
  - Polymer development team led by Professor James McGrath, an “icon” in the polymer science community
  - Spinning development team led by Professor Donald Baird, who is also highly respected by his peers
  - Main subcontractor
- University of Tennessee
  - Extensive fiber, materials, and process characterization support
- Sentech, Inc.
  - An important contributor to the development of advanced oxidation and stabilization processes
  - Leading expertise and IP rights in unique atmospheric pressure plasma processing technology
- FISIPE
  - A leading supplier of textile PAN fibers
  - Portuguese company; there are no textile PAN fiber producers active in the US
- Nanomaterials providers; several companies
  - Some do their own R&D in their material to satisfied costumer request

# Future Work



## Rest of FY10

- Continue efforts for the generation of acceptable hot-melt PAN-filaments/tows

## FY11

- Improve process efficiency and parameters to achieve a better PAN precursor
- Continue conversion of these PAN filaments/tows into carbon fibers and their evaluations
- Consideration towards scalability, more and longer filaments

# Summary



## *This year accomplishments:*

- Single filament drawn from stable melt polymer (12/2009)
- First long filament generation was achieved by PAN-Melt Spinning process (3/2010)

## *Overall Project Impact:*

- This work addresses a very important barrier in the application of carbon fiber
- This work is developing a new approach for the generation of carbon fiber PAN-precursor. This method offers a higher potential for achieving a significant cost reduction up to 30 to 50% in the generation of this precursor for carbon fiber when compared to PAN wet-spinning


Thanks!
Questions?
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