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Advanced Textiles EXPO

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Rise of Fluorine-Free Repellents for Industrial PFAS Elimination

Frank Keohan

Presentation Outline

- PFAS Concerns and Regulations
- Fluorochemicals (FC) Used in Textile Industry
- FC-DWR Benefits for Repellency and Stain Resistance
- Repellency Test Methods and Standards
- Fluorine-Free Repellents
- FC and FC-Free Material Characteristics
- Repellency Properties and Processing
- FC-DWR Development for Safer Application
- Summary

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Product Focus at Bolger & O'Hearn

- 50+ Year Old Family-Owned Company Specializing in Sustainable Textile Enhancements
- Textile Preparation and Dyeing Chemicals
  - Print Dyes
- Textile Finishes
  - Durable Water Repellents, Fire Retardants, Odor Control Treatments
- Specialty Coatings, Binders, Adhesives and Crosslinkers

bluesign® SYSTEM PARTNER

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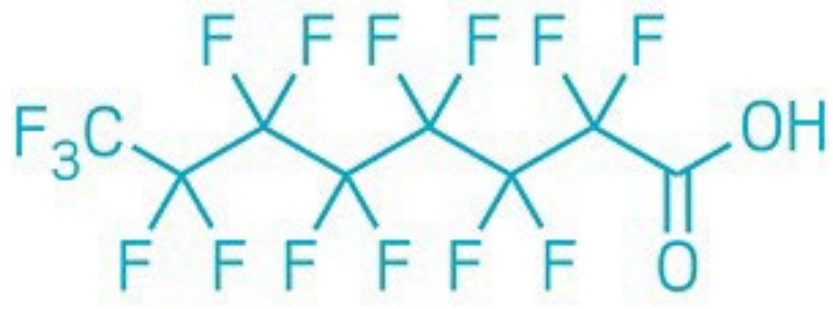
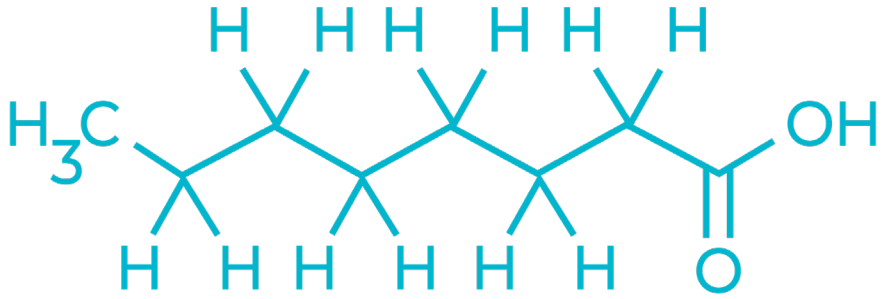
PFAS and PFAS-Based Products

- USEPA Defines PFAS as Per- and Polyfluoroalkyl Substances
- USEPA's CompTox Chemicals Dashboard now indicates there are over 9,200 unique PFAS structures
- PFAS are commonly used around the globe in non-stick cookware, food wrappers, fire-fighting foams, water vapor breathable membranes, and waterproofing or stain-repellent chemicals.
- PFAS have been used industrially for over 70 years.
- They are widely used by many industries, including aerospace, automotive, textiles, construction, cosmetics, electronics, and the military.



PFOA



Octanoic Acid

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PFAS Occurrence in Common Products

- Home
  - Non-stick Cookware
  - Food packaging
  - Plumbing
  - Clothing-water, oil, stain repellent finishes, breathable membranes
  - Cosmetics

- Outdoor
  - Roof paint
  - Firefighting foam
  - Car covers, boat covers, awnings, umbrellas

Are All Fluorinated Polymers Considered PFAS Products?

- Fluoropolymers like PTFE are technically considered PFAS
- Polymers with perfluoro groups in the backbone are considered less hazardous than perfluoroalkyl side chain types
- PTFE (Teflon) was once manufactured using PFOA but process now uses alternative fluorinated surfactants.

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Government Regulation of PFAS

- Long Chain Vs. Short Chain Regulatory Actions
  - Voluntary Phase-Out of C8 PFAS in 2015
- US EPA, FDA, CDC, Congress
- State EPAs and Legislatures
- Foreign Regulations

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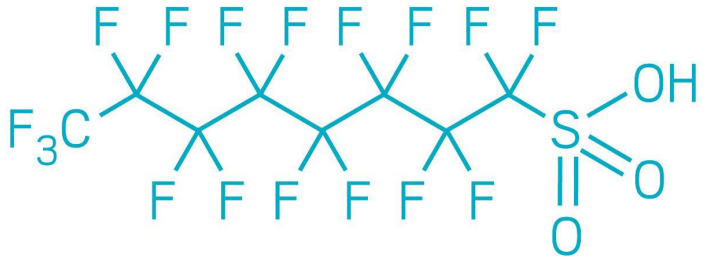
US Government Regulation of PFAS

- EPA is proposing to designate two PFAS compounds PFOA) and PFOS, including their salts and structural isomers -- as hazardous substances under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), also known as Superfund due to their hazardous nature.

- S. 2283 – PFAS Free Procurement Act
  - Senate bill would prohibit any federal agency from procuring items treated with PFOA/PFOS and give preference to suppliers of goods not treated with PFAS
  - Enactment could limit demand for repellent articles

- Slotkin Amendment
  - Affects FY 2024 National Defense Authorization Act (NDAA)
  - Would institute a two-stage procurement prohibition on various products in the military sector made with certain PFAS
  - Exception for essential function

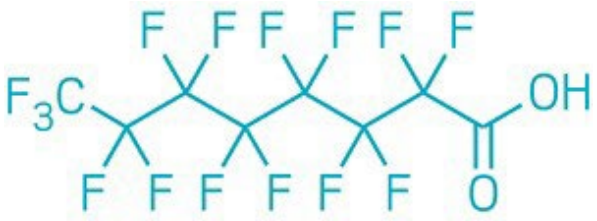
PFOA



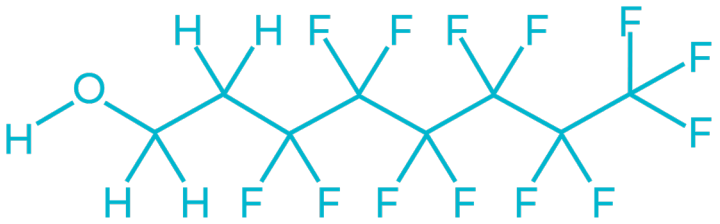
Perfluorooctanesulfonic acid

US FDA Regulation of PFAS in Food Contact

- When long-chain PFOA and PFOS were phased out under pressure from the Environmental Protection Agency, they were replaced in many products by short-chain fluorotelomers.
- Short chain (C<8) Fluorotelomers have been called the “cornerstone in replacement fluorochemistry.”
- 6:2 FTOH is used in most of the plastic coatings on food wrappers and food contact materials.
- Recent FDA studies indicate that the human health risks of 6:2 FTOH have been significantly underestimated.



PFOA



6:2 FTOH

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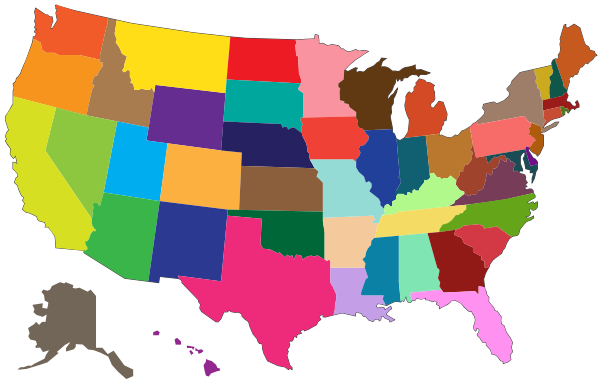
State Regulation of PFAS

- States have taken many different approaches to regulating consumer products containing PFAS. State regulations of PFAS in consumer products have principally focused on the following product sectors thus far:
  - Food Packaging, Cosmetics or Personal Care Products, Children's products, Textiles, Fabrics, Carpets, and Upholstery
  - Many regulations center around PFOA and PFOS
- 27 States have no regulations, 4 have proposed regulations, 14 have regulations covering multiple categories, and 3 have exceptional regulations
- Maine has enacted legislation prohibiting PFAS in all products by 2030.
- Beginning on January 1, 2025, the manufacture, sale, or distribution of any textiles containing more than 100 parts per million ("ppm") of PFAS will be prohibited in California

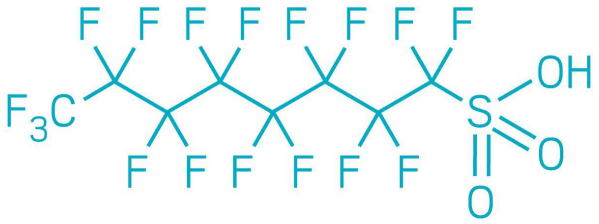


- Ref. https://www.jdsupra.com/legalnews/pfas-update-july-2022-state-by-state-3927592

Global Regulatory Climate for PFAS

- Perfluorinated carboxylic acids (C9-14 PFCAs), their salts and precursors will be restricted in the EU/EEA from February 2023 onwards following a decision taken by the European Commission
  - Exemptions for critical applications
  - Ref. https://www.jdsupra.com/legalnews/pfas-update-july-2022-state-by-state-3927592
- The regulatory situation in most Asian and Middle Eastern countries remains fluid-mostly focused on eliminating PFOA and PFOS
- Japan and China have major PFAS product manufacturing companies

PFOA



Perfluorooctanesulfonic acid

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Independent Standard Setting Organizations and PFAS

- Bluesign® has planned that from July 2023 all PFAS based chemicals will be phased out from the bluesign® FINDER and as of July 2024 all bluesign® APPROVED fabrics that are treated with PFAS formulations will be removed from the bluesign® GUIDE.

- OEKO-TEX® has issued a general ban on the use of perfluorinated and polyfluorinated alkyl substances (PFAS/PFC) in textiles, leather and footwear for the STANDARD 100, LEATHER STANDARD and ECO PASSPORT certifications.

- ZDHC: **All** the listed PFAS chemicals have been moved from Candidate to Main Manufacturing Restricted Substance List.

- Green Seal® is proposing to prohibit all chemicals classified as PFAS by the US EPA's comprehensive CompTox PFAS Master List database — an evolving list that aggregates PFAS based on environmental occurrence, manufacturing process data, and testing programs from agencies across the globe. (6/22, greenseal.org)

  - Ref. https://www.jdsupra.com/legalnews/pfas-update-july-2022-state-by-state-3927592

NGO Action on PFAS and Industry Reaction

- NGOs such as Greenpeace and US PIRG have frequently spoken out about PFAS in the environment and in commercial products
    - Negative media coverage of fluorochemicals results in decreasing demand
    - Major apparel brands have removed all PFAS from their supply chains
- Some large suppliers have ceased sales of PFAS-based repellents in North America
- Consolidation in textile chemical supply industry
- Education and messaging on differences in fluorochemicals and critical uses

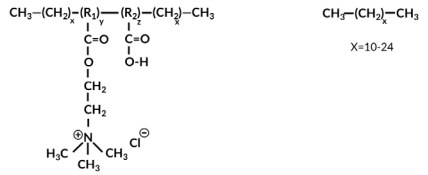
Repellent Chemistry

- Hydrocarbons
  - ➢ Hydrocarbon waxes and derivatives,
    - hydrophobic side chain
    - polymers, dendrimers

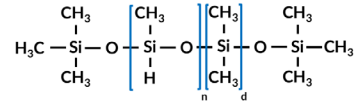
- Silicones
  - ➢ Coats fibers with silicone rubber,
    - water repellency, no oil repellency

- Fluoropolymers
  - ➢ Coats fibers with low surface energy fluoropolymer for highest level of repellency against water and oils

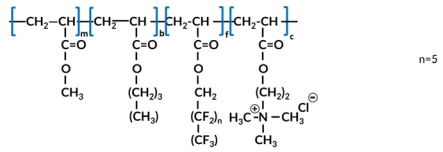
Long Chain Hydrocarbon



Silicone



Fluoropolymer



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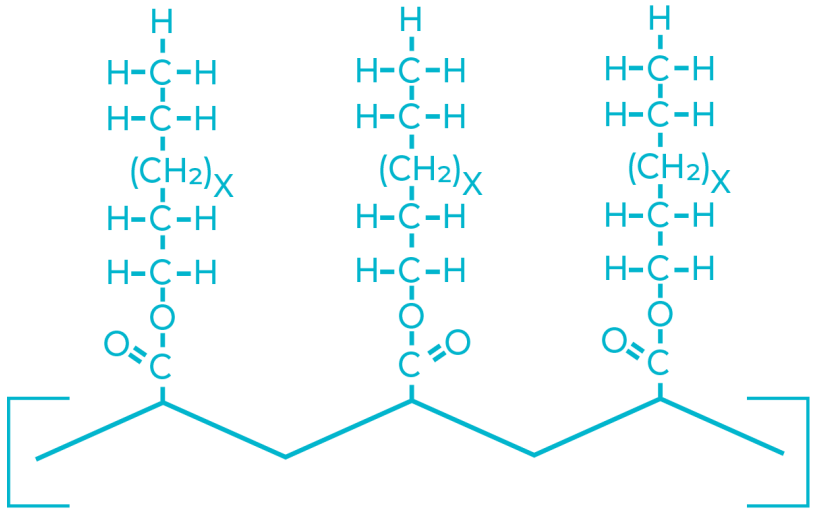
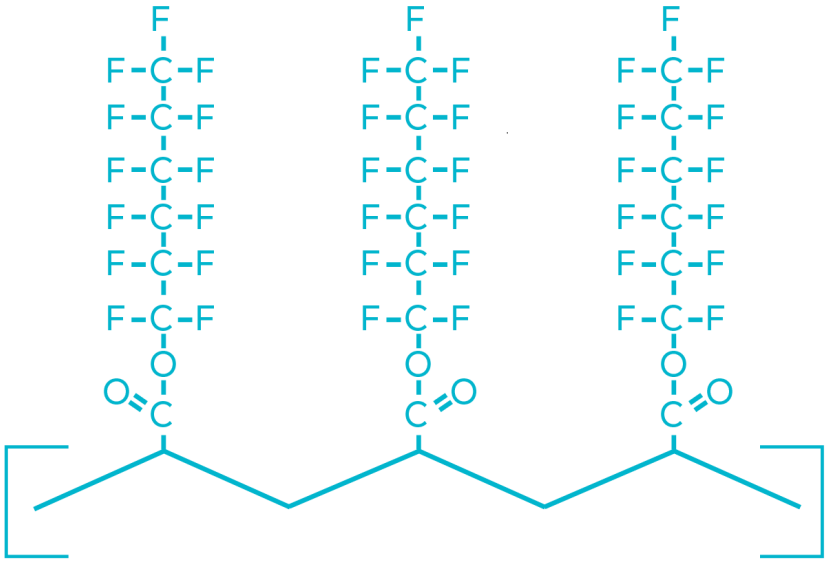
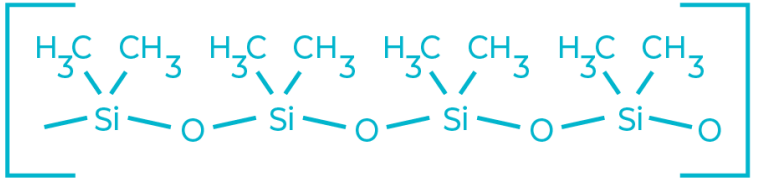
Critical Chemistry At Finished Fiber Surfaces



Hydrocarbon Side Chain Polymer



Polyfluoroalkyl Side Chain Polymer



Polysiloxane

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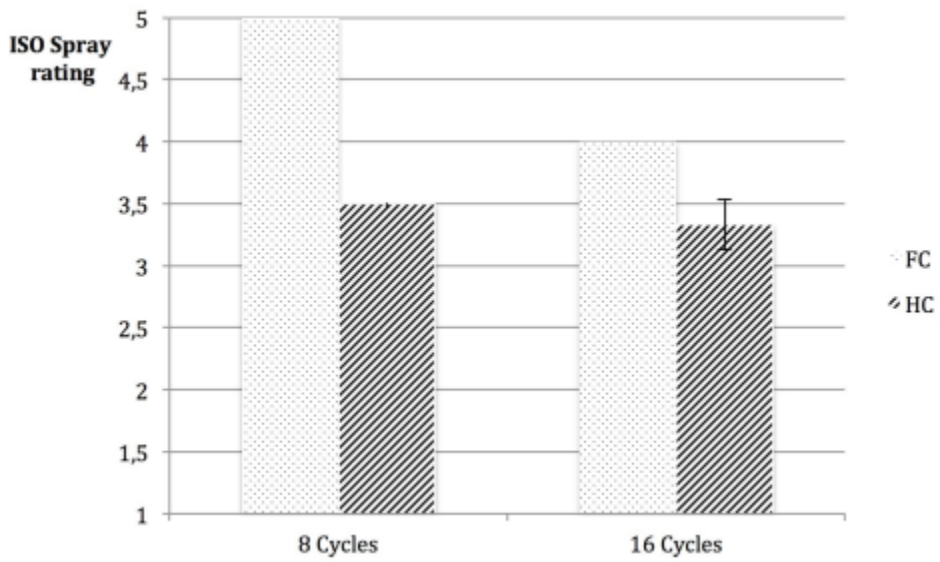
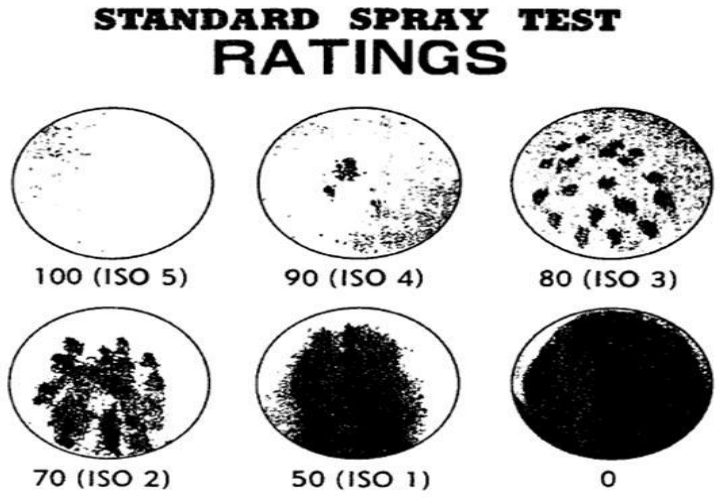
Effect of Repellent Type on UV Stability

- **DWR Finishes Resist Weathering Differently**
  - Woven polyester substrate
    - FC and hydrocarbon-based repellents
    - Both yielded 5 spray rating initially
  - UV exposure reduces water repellency more for C0-based repellents than FC-based repellents
  - Fluorocarbon polymers are more resistant to UV-induced oxidation than those based on aliphatic hydrocarbons
    - Ref. Greener Water Repellency?, Erik Göranzon and Denize Åkerblom- Swedish School of Textiles, Univerity Boras, 2013



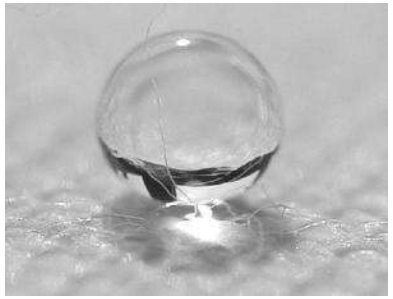
Textile Industry Repellency Testing

- Typical Industry Water Repellency Spec
  - Water Spray (AATCC Method 22)
    - Most common
    - Semi-quantitative
  - Rain Test (AATCC Method 35)
    - Used for tariff determination
    - More quantitative



Additional Repellency Test Methods

- Aqueous Liquid Repellency (AATCC TM-193)
  - Drop penetration of water/IPA solutions
- Oil Repellency (AATCC TM-193-118)
  - Drop penetration of different surface tension organic fluids
- Impact Penetration (AATCC TM-42)
  - 500 ml, 24 in drop height, witness blotter in back
  - Measures water penetration quantitatively
- Hydrostatic Pressure Test (AATCC TM-127)
  - Quantitatively measures penetration of water under hydrostatic pressure
- Bundesmann
  - Rainstorm simulator
  - Measures repellency, absorption, and penetration



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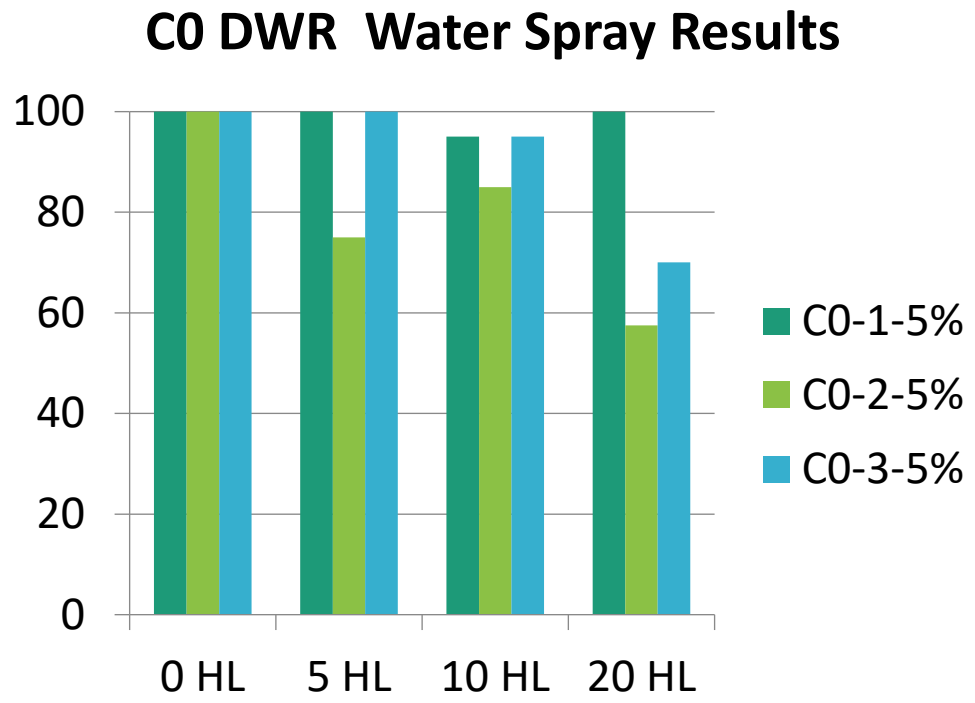
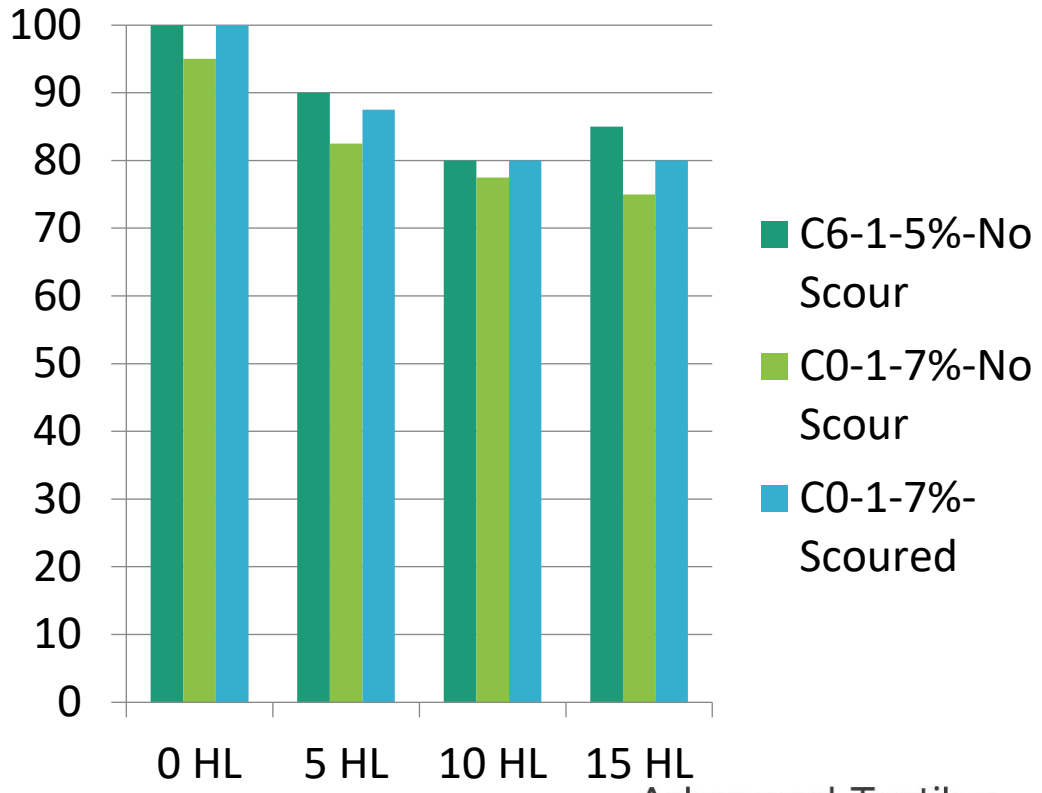
Effect of FFDWR Type on Repellency

- **All non-fluoro repellents are <u>not</u> the same for achieving water repellency**
  - Woven nylon fabric (easy to repel)
  - Applied 5% baths of three different commercial C0 DWRs and dried/cured @ 171°C for 90 sec
  - All performed well initially
  - Performance differences seen with home laundering



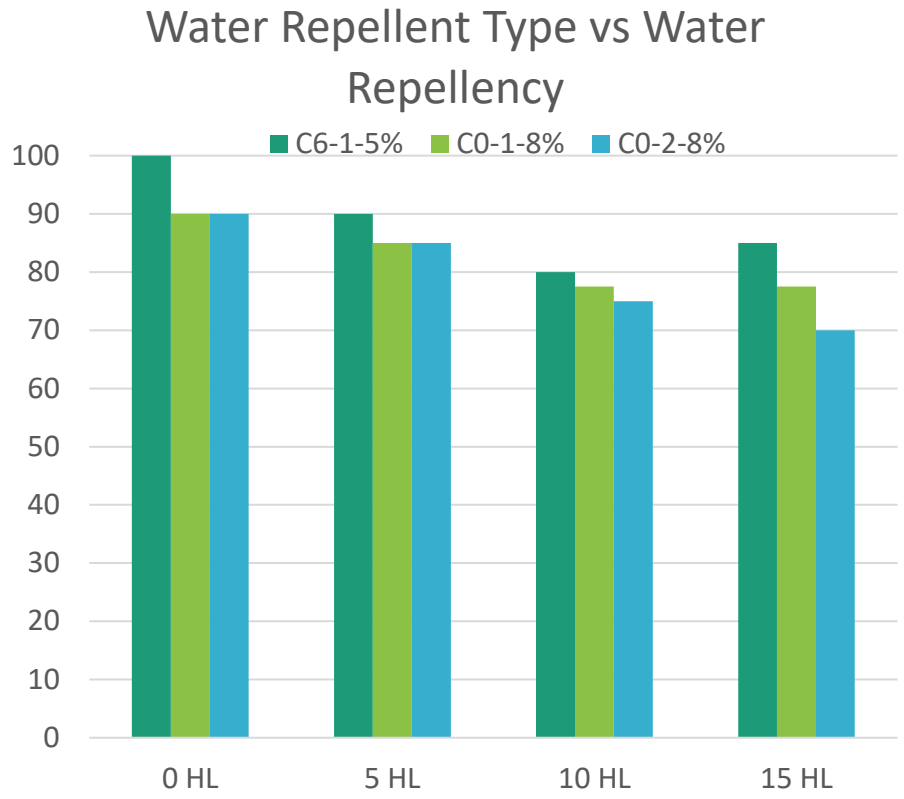
Effect of Pre-Finish Conditions on Repellency

- **Pre-finish Textile Preparation is Important for C0 DWR Performance**
  - Woven polyaramide (Nomex)
  - Simple alkaline scour used on one set of C0-DWR samples
  - Without pre-scour, C0 DWR cannot match repellency performance of C6 FC Finish
  - Scour helps both initial repellency and wash durability



Effect of DWR Type on Repellency

- **For an as-received polyaramide fiber fabric finished with different water repellents**
  - C6 FC-based repellent outperforms C0-based repellents
  - C6 FC-based repellent can be used at lower add-on compared to C0-based repellents for this substrate
  - C6 FC- repellent performance less affected by substrate



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New Capabilities for FFDWRs

- Greater biochemical content
  - Enhanced sustainability through renewable feedstocks
- Lower cure temperature requirements
  - Energy savings in application process for finishing mill
- Ability to exhibit repellency after line drying
  - Energy savings in product usage for consumer
- Outstanding water impact repellency
  - Ambient temperature drying/rain impact resistance attractive for outdoor applications

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FFDWRs Can Provide Outstanding Water Repellency

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Critical Uses for FC-Based Repellent Finishes

- Medical PPE
  - FDA sets performance standards
- Military Apparel/Equipment
  - DoD Sets performance standards
- Chemical Manufactures & Handlers
- Energy Products Manufacture, Handling and Storage
- Emergency Responder Apparel/Equipment

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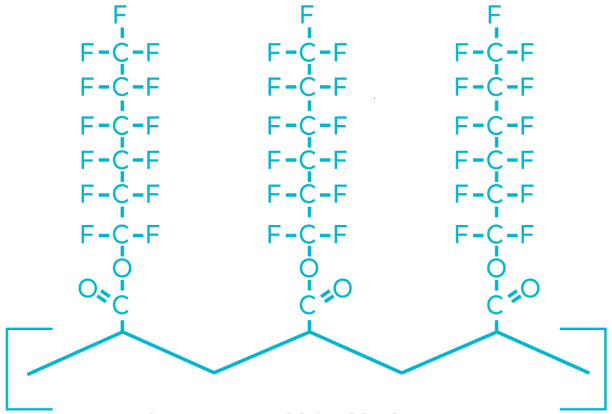
Potential Ways to Reduce Hazards from PFAS

- Reduce FCs in Finish
  - Blend with FFDWR for critical applications

- Reduce waste application liquor
  - Contained spray application
- Improve adhesion to fibers
  - Introduce more crosslinking sites into polymer backbone
  - Improve adhesion promoting bath auxiliaries
- Replace common ester link of PFA group to polymer with more hydrolytically stable bonding



Polyfluoroalkyl Side Chain Polymer

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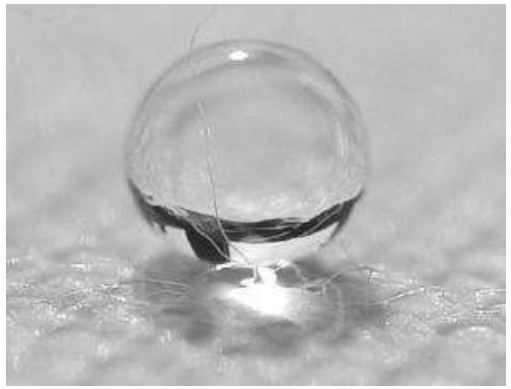
Progress on PFAS-Free Oil and Water Repellents

- University of British Columbia
  - FF silicone finish provides water repellency and some oil repellency on textiles
  - Ref. www.ecotextile .com/2020081026511



- EMD-Millipore
  - Organic polysilazane coatings
  - Thermally cure into glassy coatings with resistance to water and oils
  - Best for hard surface protection
  - Ref. www.emdgroup.com/en/brands/pm/durazane.html

Summary

- PFAS Encompass a Wide Variety of Chemicals –All containing perfluoroalkyl groups
- All **PFAS** are **Not** Created Equal-they Vary in Toxicity and Bioaccumulation
- PFAS of Increasing Concern to Public and Government Regulators
- Fluorochemicals (FC) Used in Textile Industry for broad liquid repellency
- Oil Repellency still requires FCs
- FC-DWR Provide Unique Benefits for Universal Repellency and FR compatibility
- FC and FC-Free DWRs share some Material Characteristics
- Fluorine-free Repellents are very Effective for some Applications
- Lower temperature cure and ambient temperature drying possible with FFDWRs
- Repellency Dependent on Materials, Substrates and Processing
- FC-DWR Application Engineering Proposed for Safer Usage
- FC-free Oil Repellency Possible but not yet Commercially Viable

Thank You

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