Welcome to

EMERGING TECHNOLOGIES CONFERENCE

at Advanced Textiles EXPO®

Textile Finishing Options Amid Tightening PFAS Restrictions

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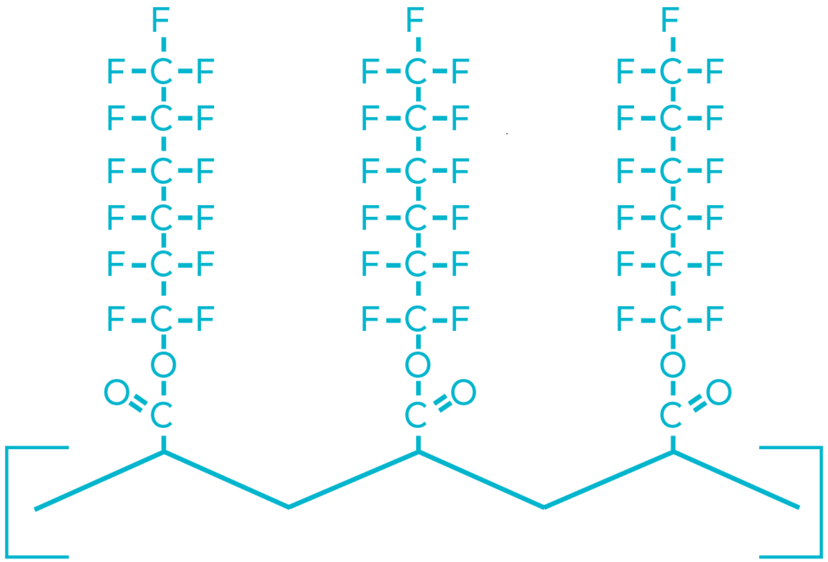
Bolger & O'Hearn/ORCO

Outline

- PFAS Concerns and Regulations
- Fluorochemicals (FC) Used in Textile Industry
- FC-DWR Benefits for Repellency and Stain Resistance
- Detection of PFAS on Fabrics
- 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

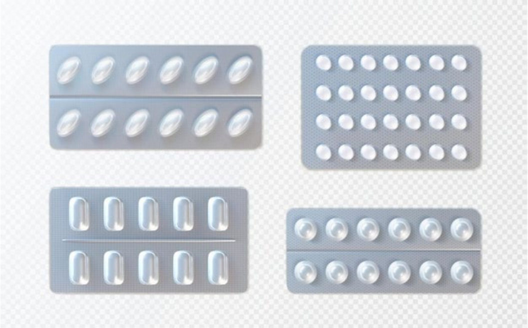


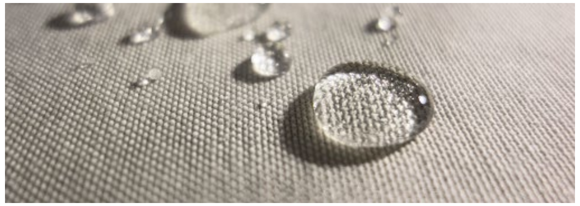
Polyfluoroalkyl Side Chain Polymer

Product Focus at Bolger & O’Hearn, Inc.

- 50+ Year Company Specializing in Sustainable Textile Enhancements
- Now part of ORCO
- Textile Preparation and Dyeing Chemicals
  - Print Dyes
- Textile Finishes
  - Durable Water Repellents, Fire Retardants, Builders
- Specialty Coatings, Binders, Adhesives and Crosslinkers

bluesign® SYSTEM PARTNER

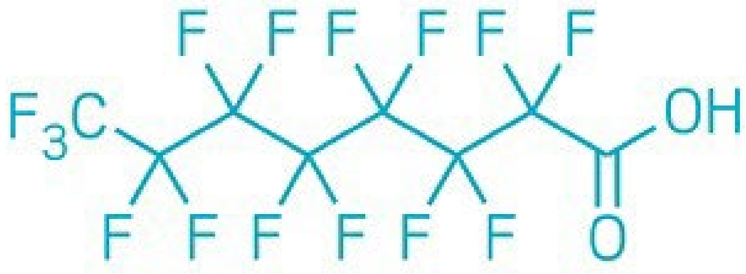




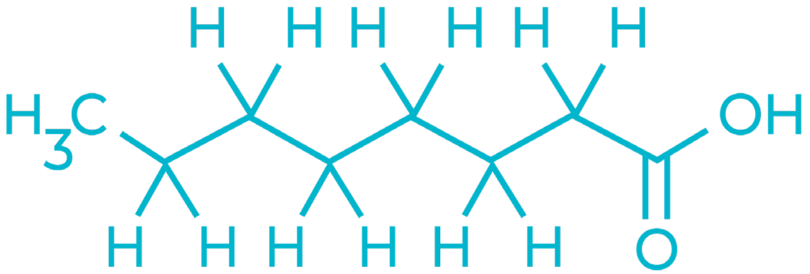
PFAS Definition and Chemical Characteristics

- USEPA Defines PFAS as Per- and Polyfluoroalkyl Substances
- PFAS bonds are extremely stable and environmentally persistent

Octanoic Acid	Perfluoro Octanoic Acid
Weak organic acid (pKa =4.9)	Stronger acid (pKa =3.8)
Good surfactant at high pH	Excellent surfactant
Readily biodegradable	Extremely persistent
Edible and readily metabolized	Bioaccumulative and toxic



PFOA



Octanoic Acid

PFAS **Occurrence** in Common Products

- **Home**
  - **Non-stick Cookware**
  - **Food packaging**
  - **Plumbing**
  - **Clothing-water, oil, stain repellent finishes**
  - **Breathable membranes for winter wear**
  - **Cosmetics**
  - **Electronics**

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

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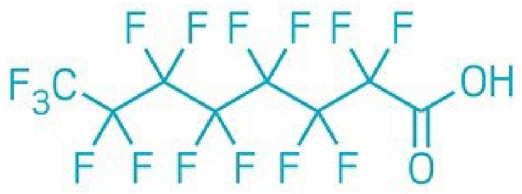
Are All Fluorinated Polymers Considered PFAS Products?

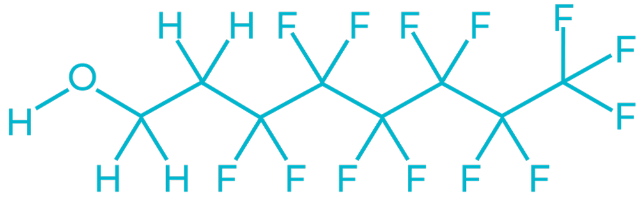
- Fluoropolymers like PTFE are technically considered PFAS.
- Polymers with perfluoroalkyl groups in the backbone are considered less hazardous than perfluoroalkyl side chain types.
- PTFE (Teflon) was once manufactured using PFOA but process now uses alternative fluorinated surfactants.

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
- 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.
- EPA recently reported that PFAS grease repellents no longer used on food wrapping products in US



PFOA



6:2 FTOH

Governmental Regulation of PFAS

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

Federal Government Regulation of PFAS

- **US Environmental Protection Agency**
  - Studies and catalogs toxic chemicals used by industry
  - Sets standards for chemicals released in environment
  - Formulates and enforces rules governing production, handling and disposal of chemicals

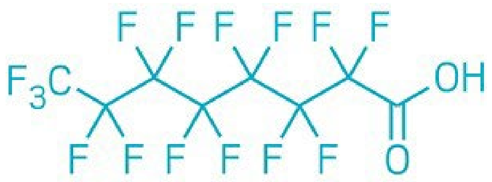
- **US Food and Drug Administration**
  - Controls substances allowed in US food supply
  - Controls substances allowed in drugs and medical devices

- **US National Institute for Occupational Safety and Health**
  - Studies chemical toxicity and formulates standards for occupational exposure

- **US Congress**
  - Enacts laws governing procurement of goods and services
  - Funds other agencies

US EPA Regulation of PFAS

- In 2024, EPA is proposing to designate nine PFAS compounds including PFOA, PFHxA 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.
    - Limit of 4 ppt for PFOA and PFOS in US drinking water
    - Limit of 10 ppt for PFNA and PFHxS in US drinking water
- EPA PFAS Reporting Requirements
    - Manufacturers must report quantities of PFAS produced or imported since 2011
    - Includes importers of fabrics or articles containing PFAS
- Waste Handling and Effluents
    - EPA developing guidance for disposal and destruction of PFAS waste



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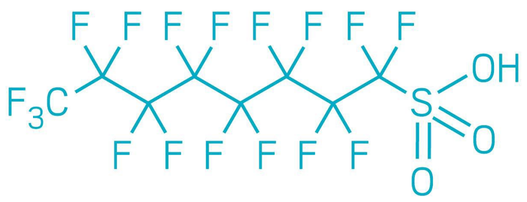
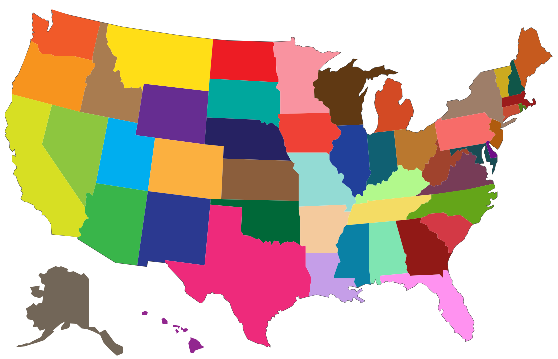


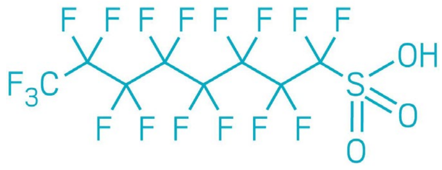
Perfluorooctanesulfonic acid

State Regulation of PFAS



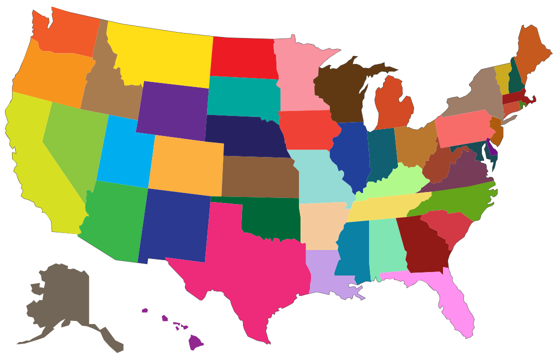
- States have taken many different approaches to regulating consumer products containing PFAS with many regulations center around PFOA and PFOS
- Some states have no regulations, some have passed new restrictions, others have proposed regulations of different severity
- **Maine** has enacted legislation prohibiting PFAS in all products by 2030.
- **Rhode Island** Passed Comprehensive PFAS Ban Act of 2024
  - Ban of textile articles (and other products) January 1, 2027. Outdoor apparel restriction as of January 1, 2029. $1000-$5000 fines for each violation of the rule
- **Minnesota** requires reporting on PFAS in products by 2026, bans non-essential uses of PFAS in all products by 2032.
- 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

PFOA

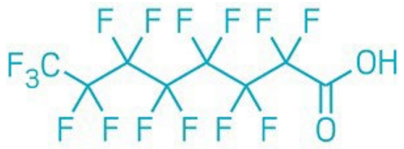


Perfluorooctanesulfonic acid

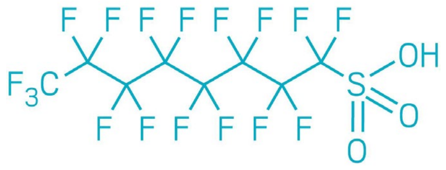
State Regulation of PFAS



- States have taken many different approaches to regulating consumer products containing PFAS.
    - 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.
- **Minnesota** requires reporting on PFAS in products by 2026, bans non-essential uses of PFAS in all products by 2032.
- 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.** Ban on PFAS in juvenile products and food packaging in effect.
- Ref. https://www.jdsupra.com/legalnews/pfas-update-july-2022-state-by-state-3927592



PFOA



Perfluorooctanesulfonic acid

Global Regulation of PFAS

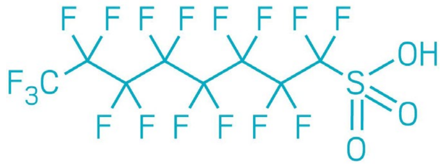
- Perfluorinated carboxylic acids (C9-14 PFCAs), their salts and precursors will be restricted in the EU/EEA from February 2023 onwards following a decision taken by the European Commission
    - Exemptions for critical applications
    - Public comment period underway

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

PFOA

- 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



Perfluorooctanesulfonic acid

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

U.S. Department of Defense (DOD) and PFAS

- The US DOD purchases a variety of textile-based products that have been traditionally manufactured using PFAS-based materials.
  - Uniforms
  - Backpacks
  - Shelters
  - Medical Items

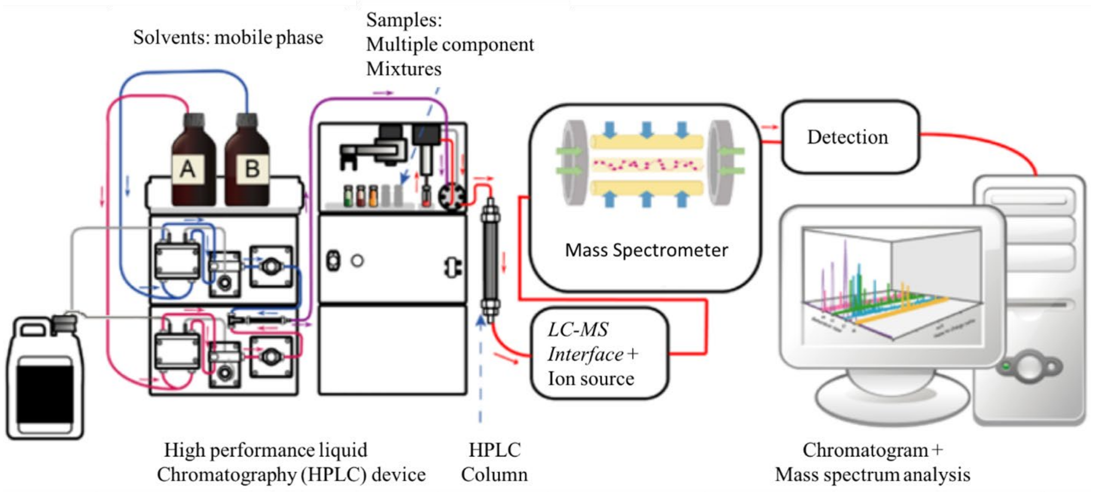
- DOD has published a formal Request For Information (RFI) regarding the use of PFAS in textile related defense materials.

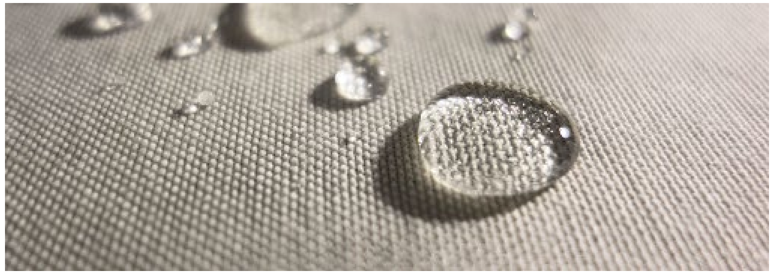
- The newly released FRI focuses on military textile uses that require oil repellency.

- Customer requests suggest move from some PFAS applications underway

PFAS Detection Methods

- Quantitative Methods
- Extraction with Organic Solvents
- Liquid Chromatography/Mass Spectroscopy
- Detection of PFAS on Fabrics
- Qualitative Methods
- Inherent Oil Repellency
  - FC-treated textiles repel water and low surface tension liquids, e.g., oils
  - C0- FC-treated textiles repel water but not organic solvents or oils
  - Isopropyl Alcohol (IPA)/Water solutions can wet C0-finished surfaces but repelled by FC-finishes



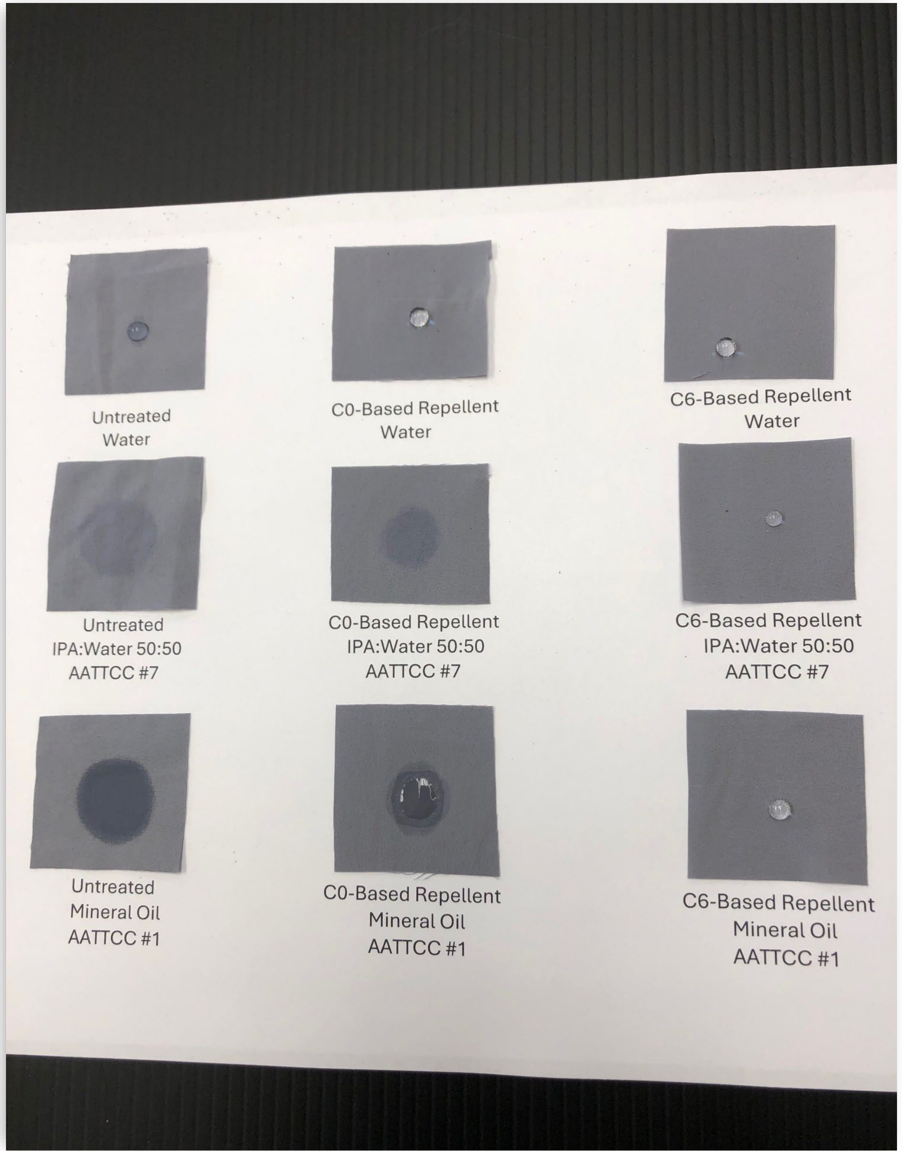


Qualitative PFAS Finish Detection on Textiles

- Water drop repellency shows fabric is finished with a repellent

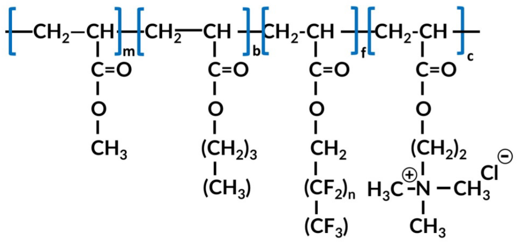
- 50:50 Water:IPA drop repellency can discern between PFAS repellents and C0-based repellents (AATCC 193-liquid #7)

- Mineral oil can also be used to discern between PFAS repellents and C0-based repellents but is difficult to remove from a fabric after testing



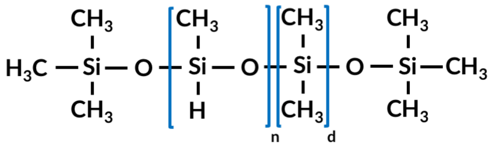
Repellent Chemistry

Fluoropolymer

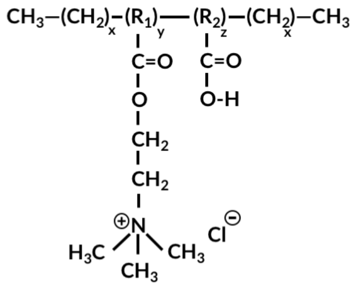


n=5

Silicone



Long Chain Hydrocarbon

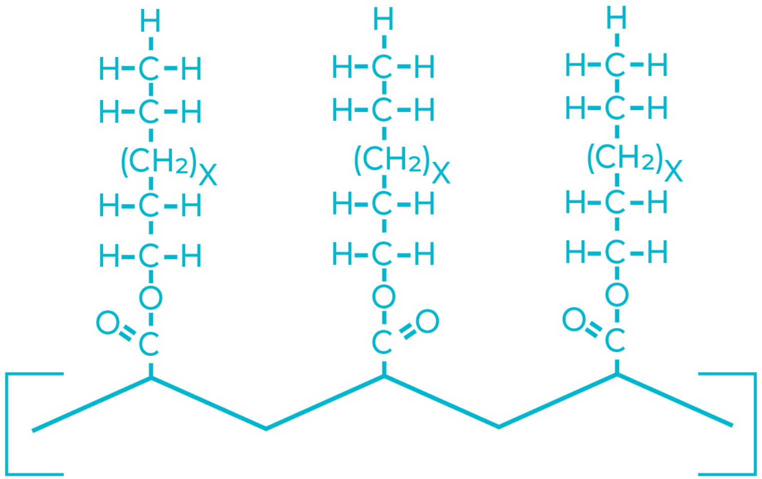


$CH_3-(CH_2)_x-CH_3$

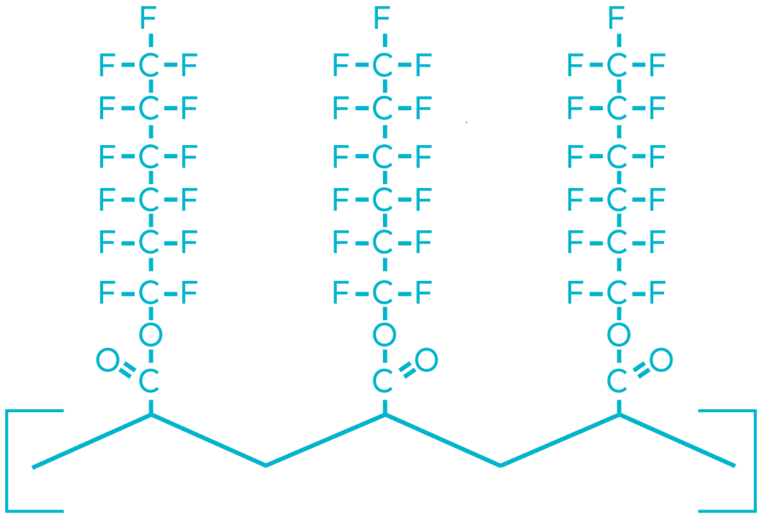
X=10-24

- Mostly delivered from water emulsions
- All coat fibers with hydrophobic layers
- All provide water repellency
- Only fluorochemicals provide water and oil repellency

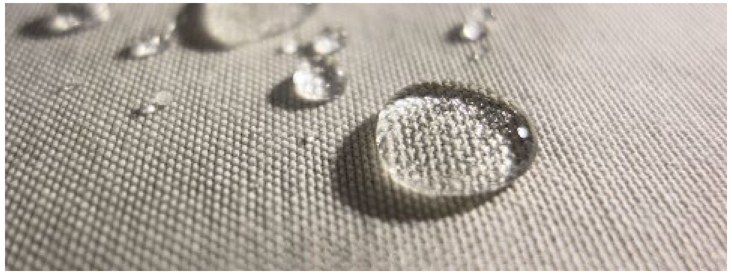
Critical Chemistry At Finished Fiber Surfaces

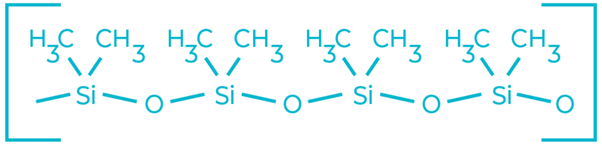


Hydrocarbon Side Chain Polymer



Polyfluoroalkyl Side Chain Polymer



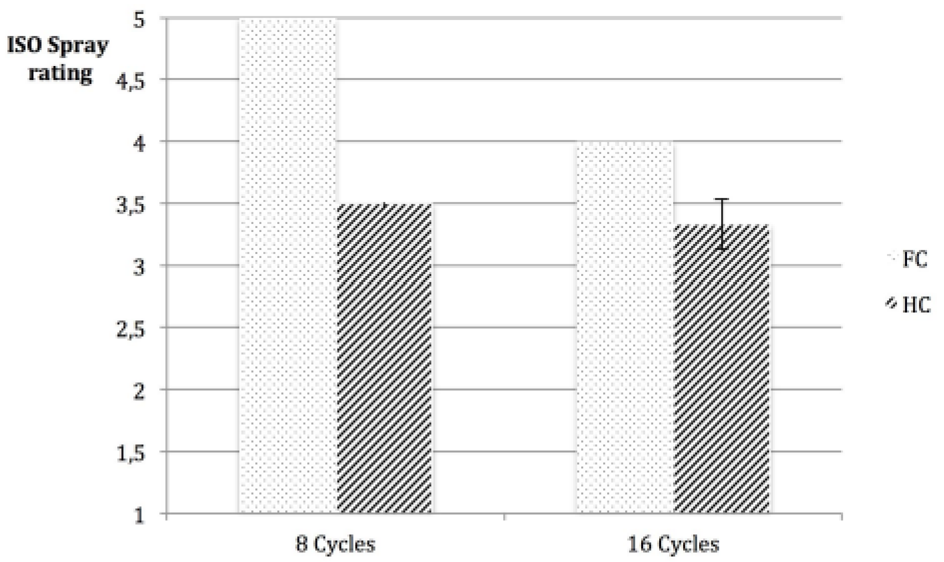


Polysiloxane

- Hydrocarbon and perfluoroalkyl types need heat to provide optimal repellency
- Silicones do not need reheating after wetting out to restore repellency

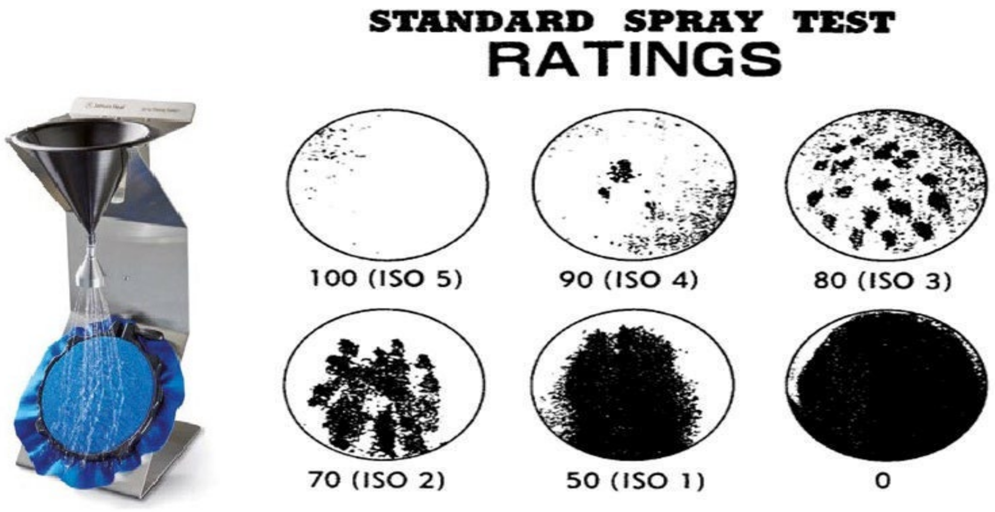
Effect of Repellent Type on UV Stability

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



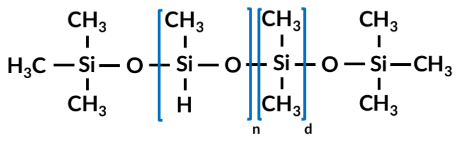
Additional Repellency Test Methods

- 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

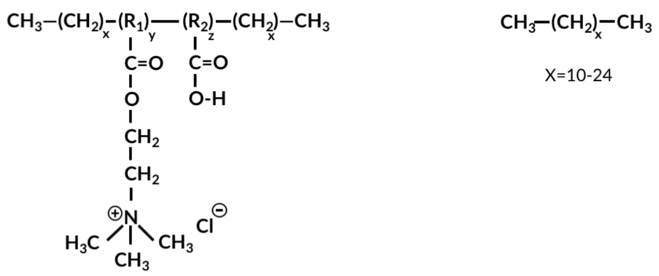
Current Alternatives to PFAS-Based Repellents

- Silicones
  - PDMS fiber coatings don’t need heat exposure for repellency regeneration
- Hydrophobic Waxes
  - Least expensive
  - Least durable
  - Need heat exposure to regain repellency after wetting
- Hydrophobic Side Chain Polymers
  - Analogous to PFAS-side chain polymer repellents
  - Need heat exposure to regain repellency after wetting

Silicone

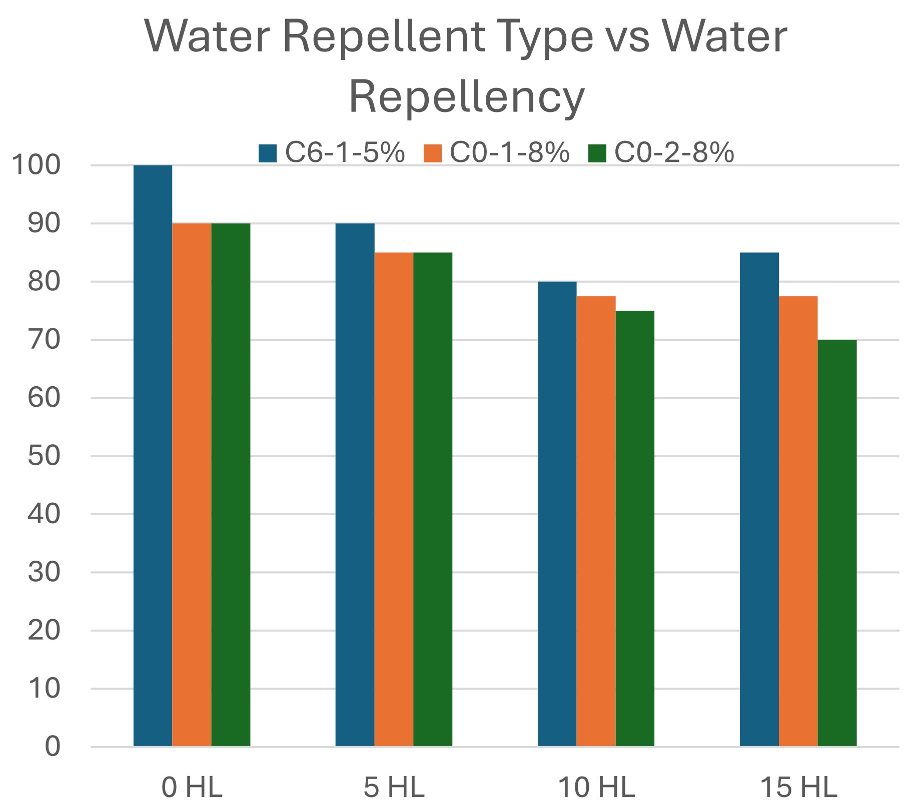


Long Chain Hydrocarbon



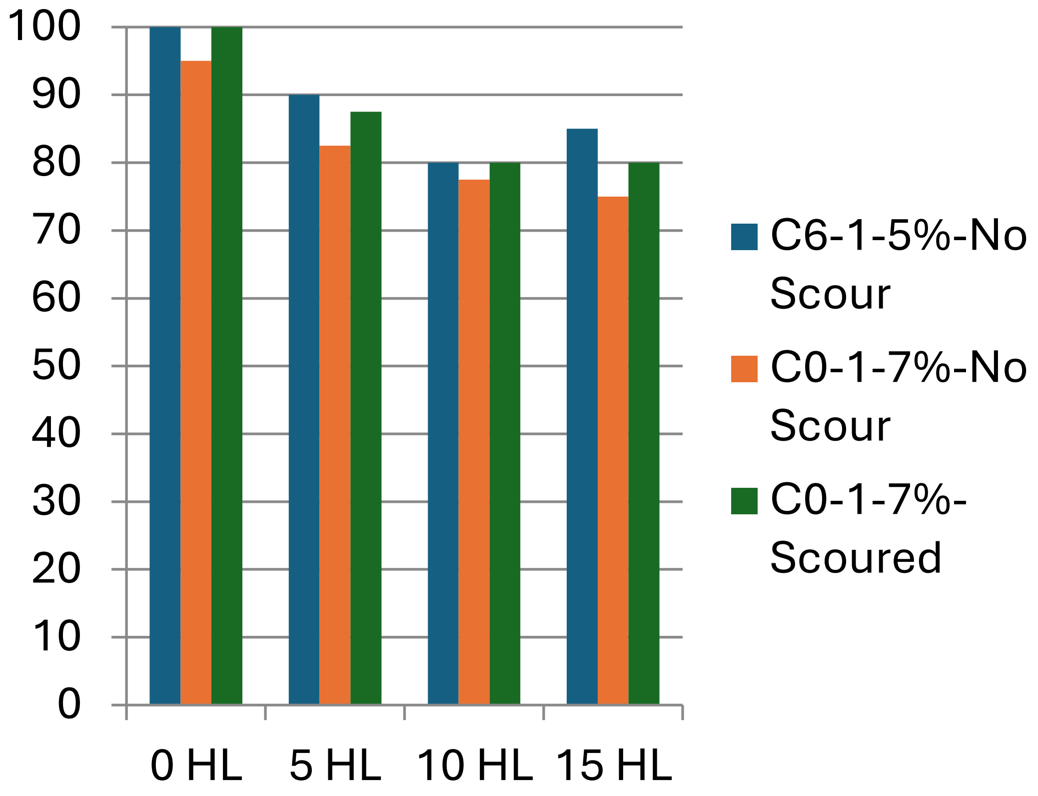
Effect of DWR Type on Repellency

- **For a 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



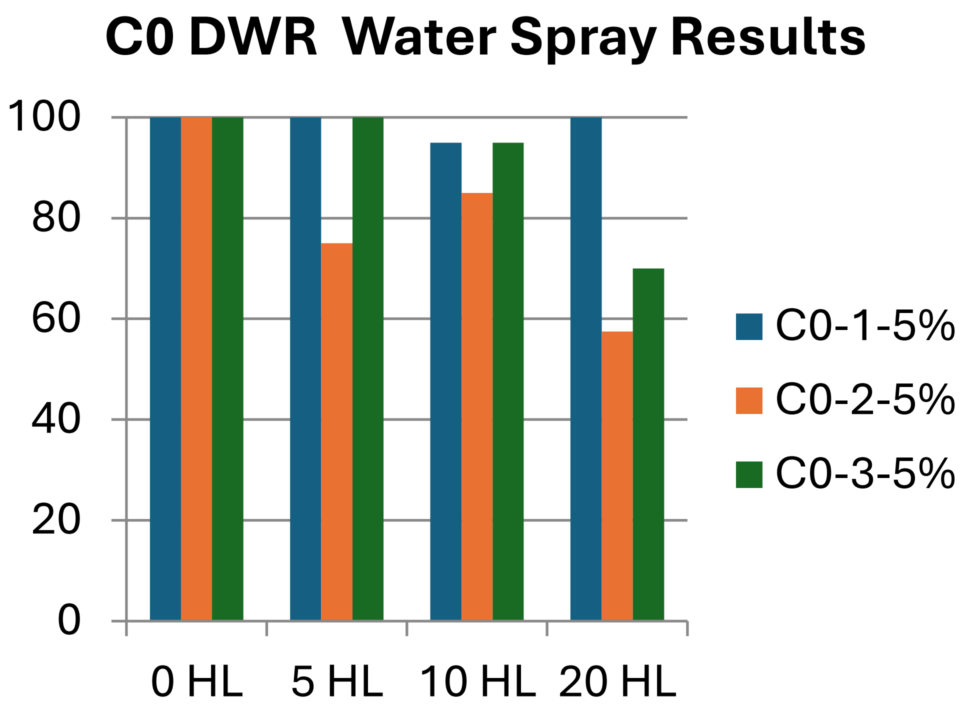
Effect of Pre-Finish Conditions on Repellency

- **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 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



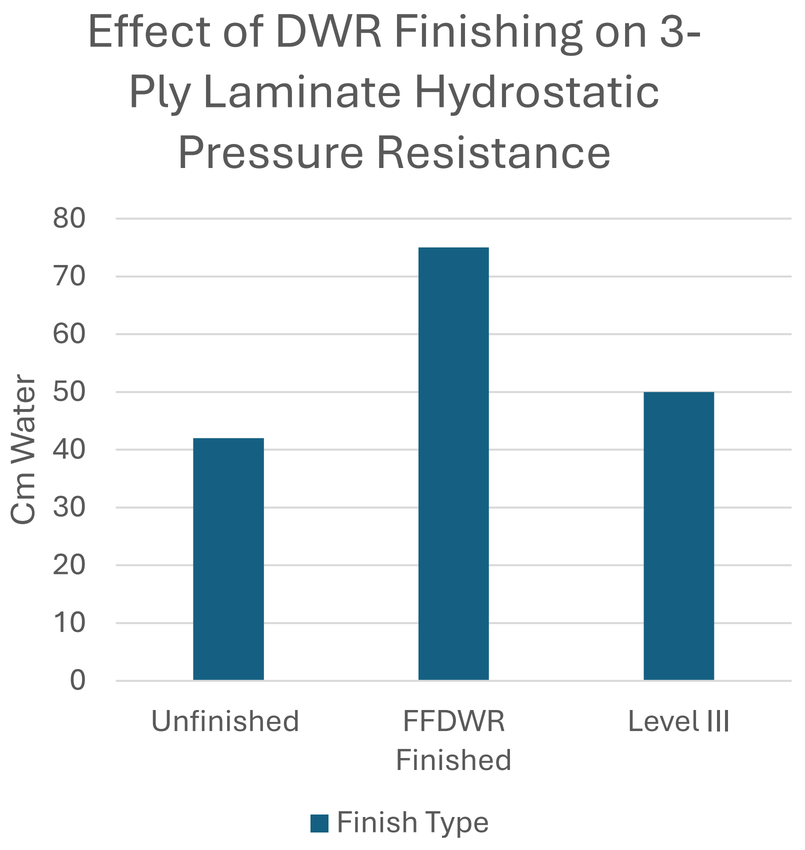
Applying Repellent Technology to Provide Enhanced Barrier Properties

- Nonwoven Textile Mill Customer Sought to Produce a 3-ply Laminate that Passes Level 3
  - Nonwoven PES Outer Layer
  - Meltspun PP Nonwoven Middle Layer
  - Woven PES Scrim Inner Layer

- Applied DWR to PES Outer Layer
- 3-Ply System Passed Level Water Barrier Requirements for Single-Use PPE Articles

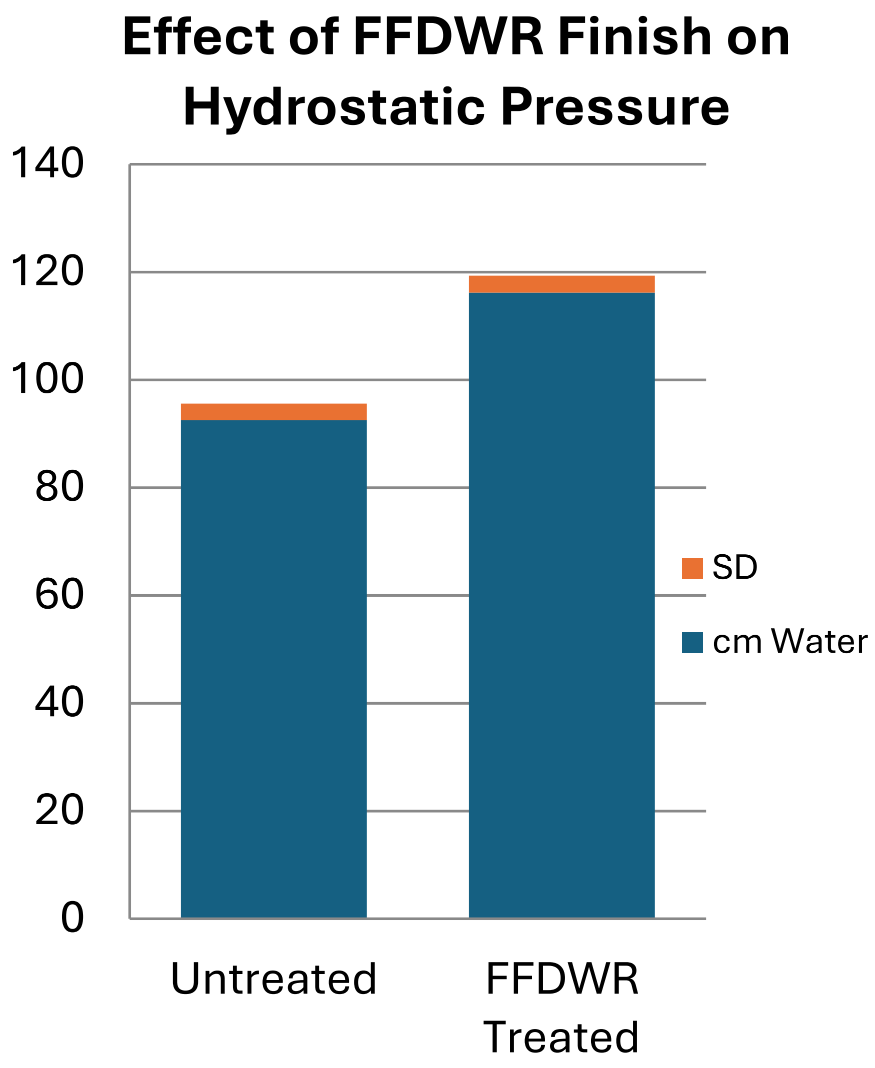
Fluorine-Free Treatment of Nonwoven PP Textile for Improving Barrier Properties

- Objective: Meet Level III Water Barrier Specification for 3-Ply Laminate
- 3-Ply Barrier
  - Outer Spunbond PP NW-25 GSM
  - Middle Meltblown PP NW-26-GSM
  - Inner Spunbond PP NW
- Untreated and FFDWR-Finished Outer Layer Samples Meet AATCC 42 (≤ 1.0g Water Requirement)
- Untreated Outer Layer Samples Meet Level II AATCC 42 TM-127 (Hydros ≥ 20 cm water) but fail Level III (≥ 50 cm water)
- FFDWR Finishing Outer Layer Raises Hydros to ≥ 50 cm water Meeting Level III Requirements



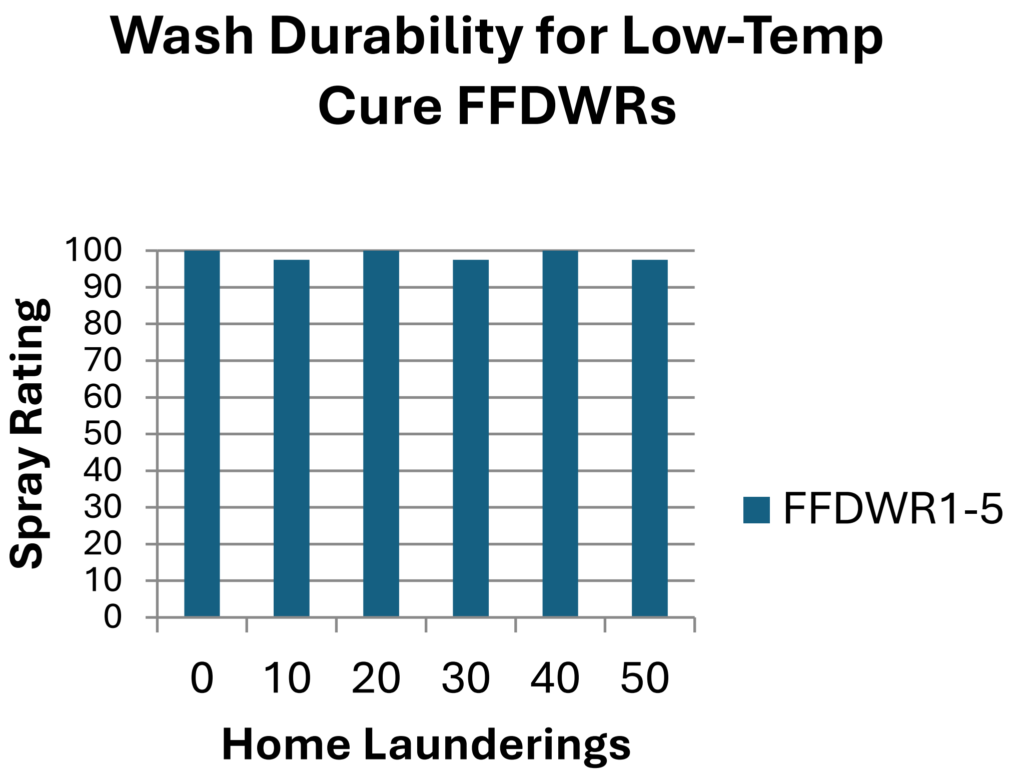
Fluorine-Free Treatment of Nonwoven PP Textile for Improving Barrier Properties

- PP Textiles are Inherently Hydrophobic
- FFDWR Finishing Can Increase Hydrostatic Pressure Resistance
- Processing Conditions Important
- Low temperature DWR Cure Needed for Certain Textiles



Wash Durability for Low Temperature-Curing FFDWRs

- **Excellent Wash Durability Possible with Selected FFDWRs**
  - Woven 100% Polyester
  - 5% FFDWR bath pad-applied and air-dried
  - Only cure in clothes dryer cycles (c.a. 170°F)

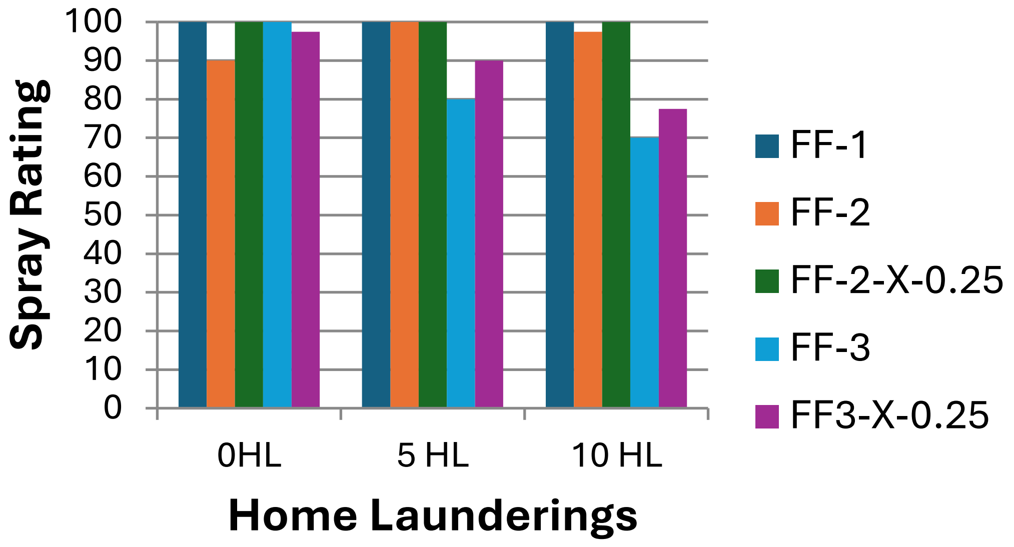


Effect of Crosslinker Auxiliary on Low Temperature-Curing FFDWRs Performance

- Woven 100% Polyester
- 5% DWR bath pad-applied
- Finished samples cured for 2 min @ 100°C

- **Repellency Durability Improved by Addition of Low Temperature-Activate Crosslinker**

Wash Durability for Low-Temp Cure FFDWRs

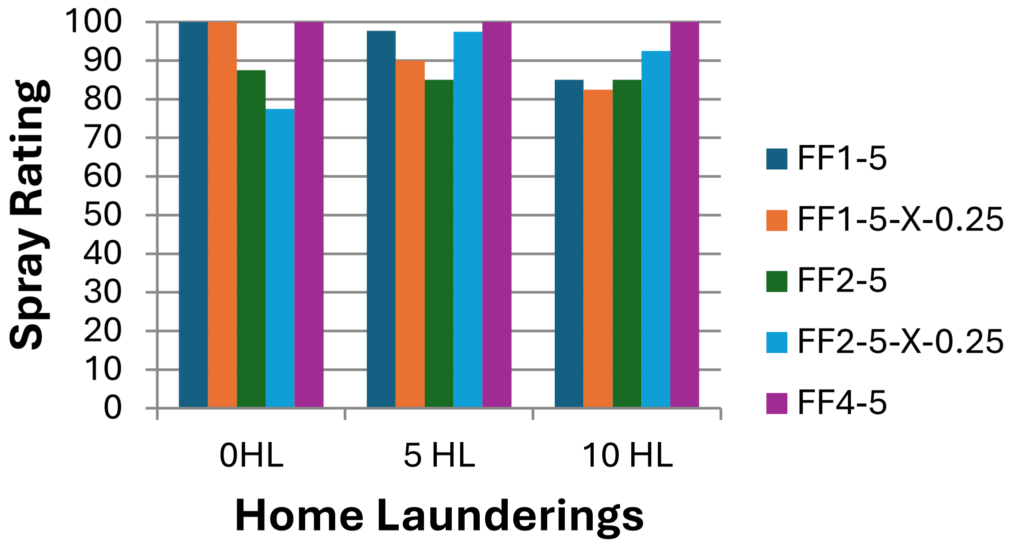


Effect of Crosslinker Auxiliary on Low Temperature-Curing FFDWRs Performance

- Woven 100% Polyester
- 5% DWR bath pad-applied
- Finished samples cured for 2 min @ 80°C

- **Addition of Low Temperature-Activate Crosslinker Less Effective for 80°C Cure**

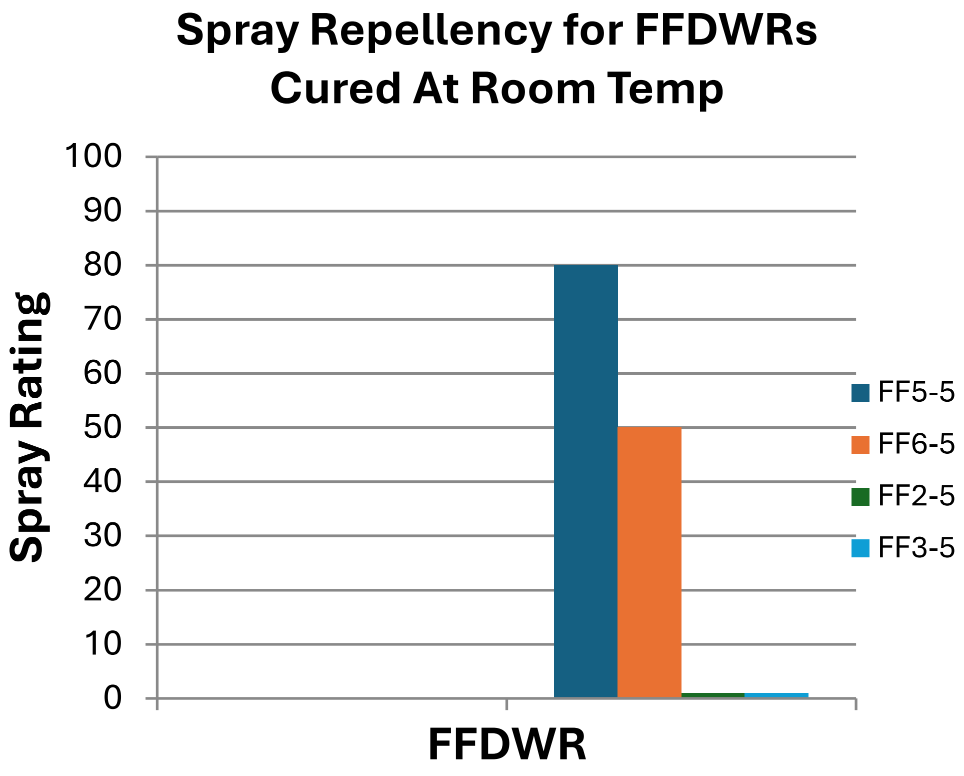
Wash Durability for Low-Temp Cure FFDWRs



Room Temperature-Curing FFDWR Performance

- Woven 100% Polyester
- 5% DWR bath pad-applied
- Finished samples cured for 24 Hour @ 22°C

- **Selected FFDWRs Show Moderate Water Repellency After RT Cure**

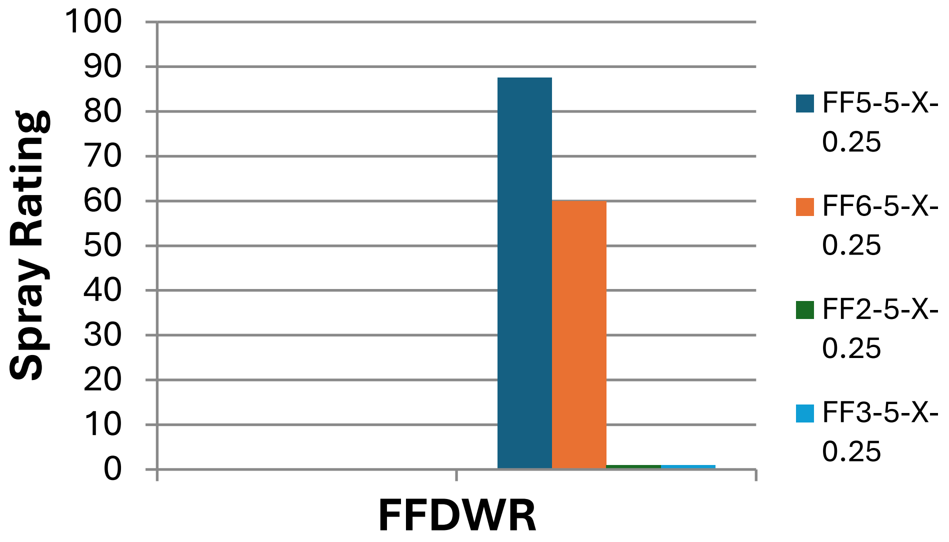


Effect of Added Crosslinker on RT-Curing FFDWR Performance

- Woven 100% Polyester
- 5% DWR bath pad-applied
- Finished samples cured for 24 Hour @ 22°C

- **Selected FFDWRs Show Improved Water Repellency After RT Cure**

Crosslinking Effect for Room-Temp Cure FFDWRs



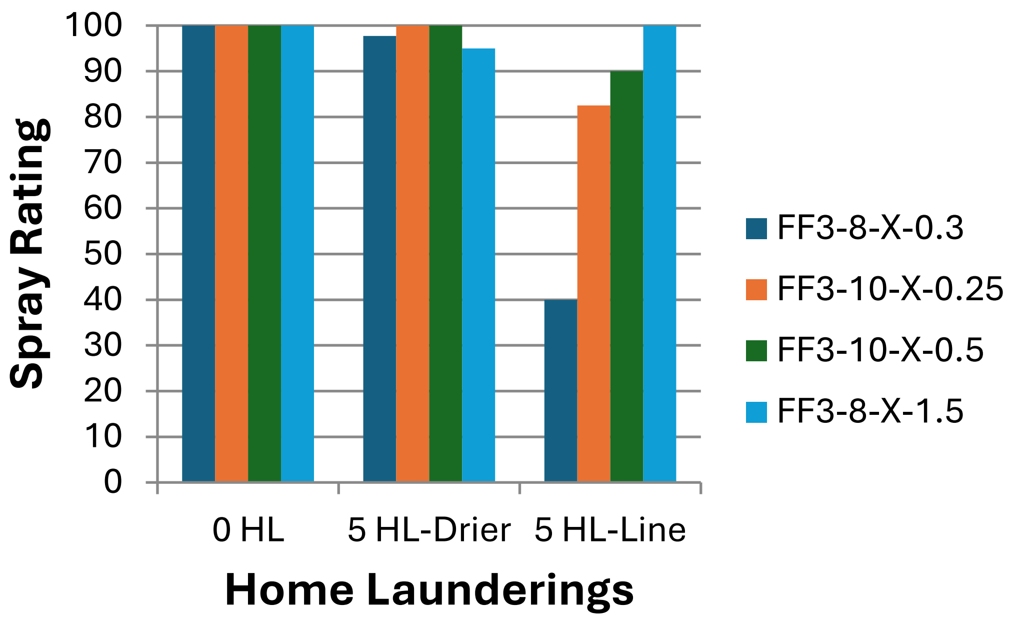
FFDWRs Can Provide Outstanding Water Impact Resistance

Effect of Laundry Drying Method on FFDWR Performance

- Woven 100% Polyester
- DWR bath pad-applied
- Finished samples cured for 90 sec @ 170°C

- **Addition of Low Temperature-Activated Crosslinker Improves Line Dry Durability**

Wash Durability for FFDWRs



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

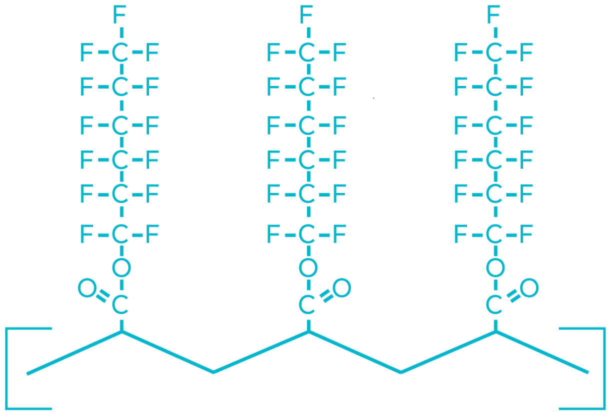
Potential Ways to Reduce Hazards from PFAS

- 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

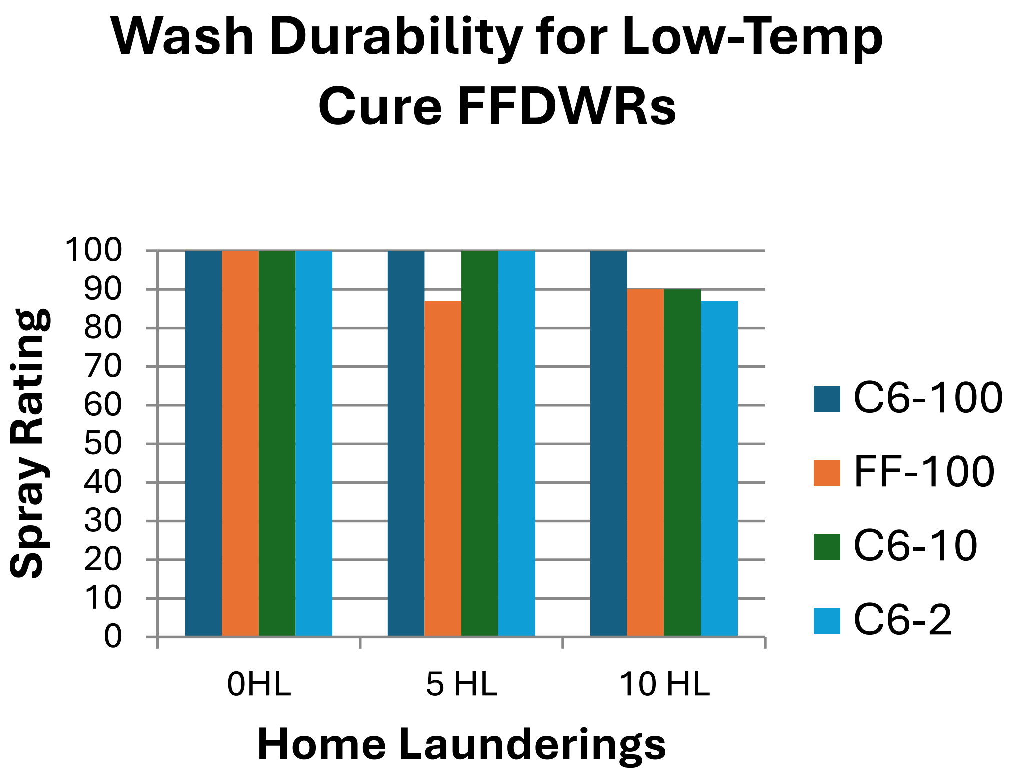


Polyfluoroalkyl Side Chain Polymer

Effect of C6 Content on Water Repellency for Low Temperature-Curing FFDWRs

- Woven 100% Polyester
- 5% DWR bath pad-applied
- Finished samples cured for 2 min @ 100°C

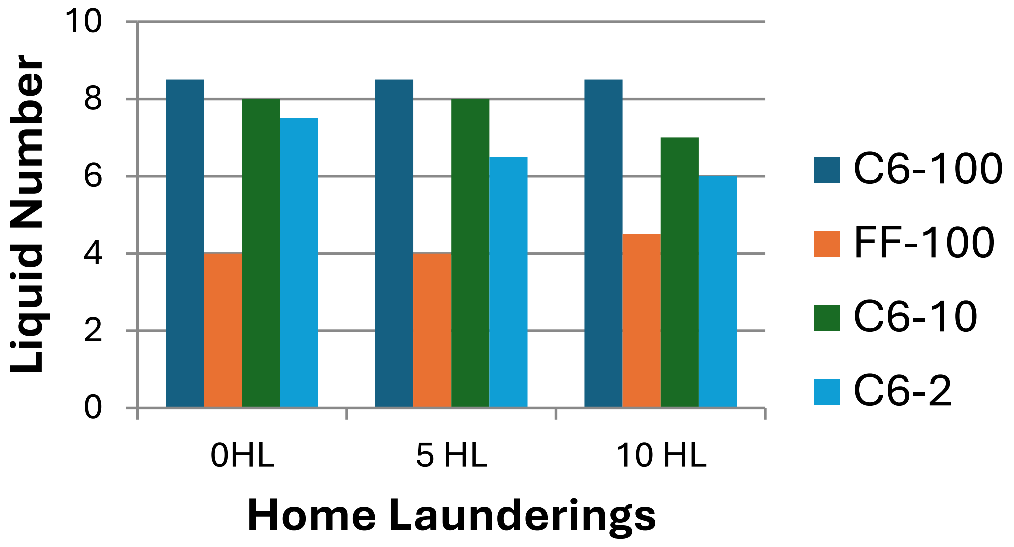
- **Excellent Repellency and Durability Possible with FFDWRs and C6 Blends**



Effect of C6 Content on Liquid Repellency for Low Temperature-Curing DWRs

- Woven 100% Polyester
- 5% FFDWR bath pad-applied
- Finished samples cured for 2 min @ 100°C
- **Excellent repellency and durability possible with FFDWRs and C6 Blends**
- **2% C6 provides useful alcohol resistance**

Aqueous Liquid Repellency for Low-Temp Cure DWRs



Potential Fluorine-Free Oil and Water Repellents

- FF brush-polysiloxane copolymer silicone finish provides water repellency and some oil repellency on textiles
  - Oil repellency is highly dependent on fabric structure
  - Level of oil repellency similar to C4 fluorochemical finish
  - Ref. Cheng, et al, Progress in Organic Coatings, 183, October, 2023, 107726
- 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 Potential
- PFAS of Increasing Concern to Public and Government Regulators
- Fluorochemicals (FC) Used in Textile Industry for broad liquid repellency
- Fluorochemicals can be analyzed using solvent extraction/instrumental analysis
- Qualitative tests can be used to broadly identify fluorochemical treatment
- 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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