



Safer Treatments to Create Water & Oil Repellent Fabrics

By J. Michael Quante



THE STORY SO FAR

It seemed like a dream come true: a fabric treatment that imparted repellency to liquid exposures. Discovered in 1938 at DuPont, PFAS (per- and polyfluorinated alkyl substances), also known as “forever chemicals” due to their persistence, were touted as an inert, stable treatment, with polytetrafluoroethylene (PTFE) initially used in consumer products for making non-stick cookwear.¹ PFAS have since found extensive use in many industries, such as the manufacture of water and oil repellent textile products, including protective textiles (e.g., firefighting turnout gear), carpets, and outdoor/sportswear clothing.²

It wasn't until the 1960s that concerns began to arise over the effects of PFAS on human and ecological health. One worrisome compound is perfluorooctanoic acid (PFOA, C8), which was suspected of causing health problems, and contaminated ground water near a PFAS manufacturing plant in Parkersburg, WV, USA.³ Another persistent water pollutant is perfluorooctanesulfonic acid (PFOS), an earlier key ingredient in a well-known stain repellent textile treatment that was replaced and is no longer produced in the United States but is still manufactured in some other countries.²

Today, there are an estimated 10,000 PFAS compounds present in the biosphere, making it difficult to pinpoint the toxicity of many individual PFAS compounds.⁴

PFAS IN TEXTILE APPLICATIONS

Two types of PFAS are used in textile finishing: polymeric (e.g., PTFE) and non-polymeric (e.g., PFOA and PFOS). The former includes finishes applied to

textiles, while the latter are used as low molecular weight polymer processing aids (i.e., emulsifiers) during treatment with polymeric PFAS. Many non-polymeric PFAS, including the ammonium salt of hexafluoropropylene oxide dimer acid (HFPO-DA, GenX), are not only persistent, mobile, and toxic, but also water soluble, accumulating in surface water, groundwater, and soil.⁵ Four non-polymeric PFAS—PFOA, PFOS, perfluorohexanesulfonic acid (PFHxS), and perfluorononanoic acid (PFNA)—have even been found in rainwater, often above current regulatory limits.⁶ Much attention has been focused on banning these emulsifiers, as they are widely distributed and detrimental to human and environmental health.

Polymeric PFAS impart water and oil repellency to textiles. PFOA surfactant has been used for the emulsion polymerization of PTFE, but its use has been discontinued by some manufacturers.

TESTING

Testing for PFAS is a complex subject, partially due to the patchwork of regulatory rules at state and national levels in many countries. Both the United States (US) and the European Union (EU) are grappling with how best to screen and analyze for PFAS. A key question: should use of all PFAS be banned in textiles or just the compounds that are strongly suspected of causing human/ecosystem health issues? This is a contentious issue, with proponents⁷ and opponents⁸ staking out claims.

In the US, many states have taken the lead in banning the use of some or all PFAS in products.⁹ Several international organizations have developed, or are developing, standards and guides to use for determining PFAS content.

ASTM International created a new subcommittee (F15.81) to develop PFAS standards for consumer products.¹⁰ Jeff Stull, co-chair of F15.81 and president of International Personal Protection Inc., is involved in developing a new, comprehensive PFAS standard guide, similar to the ASTM E3302-22 Standard Guide for PFAS Analytical Methods Selection,¹¹ used for the determination of PFAS in environmental samples.

“This guide is intended to identify methods that can be used to measure PFAS in different ways in these different kinds of products,” says Stull. This will be more than just a list of methods. It will include test setups, including the limitations and constraints that may be encountered in performing the tests and analyzing the subsequent results.”



“We hope that this guide will help inform manufacturers [as to] how they evaluate products for compliance to standards..., help consumer groups..., [and] inform regulatory bodies,” says Stull. These recommendations will not address regulatory limits. Preparation methods for analyses of different sample types will be proposed, as well as a comprehensive approach to applying and interpreting the results. First ballots on this guide at the ASTM subcommittee level will be started in June 2023.

On March 30, 2023, the AATCC Chemical Applications Interest Group held a discussion on PFAS testing with US Environmental Protection Agency (EPA) Environmental Engineer Doruntinë Rexhepi and Zhanyun Wang from Empa (Swiss Federal Laboratories for Materials Science and Technology). Rexhepi discussed EPA’s Effluent Guidelines Program Plan 15 (Plan 15) focused on the Textile Mills Point Source Category (40 CFR 410).¹² The Plan 15 annual review “describes analyses, studies, and rulemakings related to effluent limitations guidelines and pretreatment standards (ELGs).”^{13,14}

In summary, “EPA has collected additional data on PFAS use and discharge from textile mills from technical literature, textile manufacturing companies, EPA regions, and state and local wastewater regulatory

authorities. Based on this new information and *limited* data collected and reviewed, EPA announced its intent **to expand the scope** of the existing Textile Mills detailed study to include collecting data on PFAS use and discharge through a mandatory survey from this industry.¹⁵ EPA is also developing two new Clean Water Act (CWA) analytical methods applicable to PFAS: Draft Methods 1633¹⁶ and 1621.¹⁷

Zhanyun Wang spoke on forthcoming EU REACH (Registration, Authorization, and Restriction of Chemicals) restrictions on PFAS. He first mentioned that in March 2023, the EPA announced proposed drinking water restrictions for six PFAS that will be legally enforceable under the Safe Drinking Water Act.¹⁸ This was followed by a discussion of the January 2023 restriction submission made by five national authorities (Denmark, Germany, the Netherlands, Norway, and Sweden) to the European Chemicals Agency (ECHA) for possible inclusion into REACH.

ECHA’s scientific committees are currently evaluating the submission during a six-month consultation period beginning in March 2023. During this process, these committees will formulate their opinions, which will then be adopted and then sent to the European Commission for a decision on potential restrictions.¹⁹

PFAS and Protecting Firefighters

Firefighter gear must provide both comfort and protection to the wearer to be effective and safe. But what happens when you need to be protected from the protection? You balance tradeoffs.

This is the puzzle that researchers face in evaluating the impact PFAS and alternatives have on firefighter health and safety. Bryan Ormond, assistant professor, Textile Protection and Comfort Center (TPACC) at the Wilson College of Textiles, North Carolina State University has a lot of experience working with firefighters and their gear.

“PFAS and firefighters is a very complicated topic,” says Ormond. “If you look at all different routes of exposure, not just the gear itself, the fire, the [firefighting] foams, the occupational exposure... we don’t quite understand everything. But that shouldn’t stop us from moving forward... how do we move forward with alternative finishing and products?”

Ormond emphasizes the importance of proper firefighter training to prepare them for understanding the benefits, limitations, and tradeoffs of using non-fluorinated treatments instead of PFAS in their gear. “As much as we can, keeping the same level of performance in the gear they’re used to, but then limit their exposures, maybe by changing the way we do things.”

For the time being, under the “essential use” regimen, some PFAS may continue to be used in firefighter gear until the need for its protective properties are adequately addressed by new alternative treatments.

Ormond will be speaking at the July 2023 AATCC PFAS program.



Also discussed during the meeting was the concept of “essential use.” To summarize, “A phase-out of many uses of PFASs can be implemented because they are not necessary for the betterment of society in terms of health and safety, or because functional alternatives are currently available that can be substituted into these products or applications.”²⁰

Hohenstein Institute is an international testing organization providing services to textile, leather, and footwear manufacturers, suppliers, and other interested parties.²¹ They provide the expertise to evaluate textile PFAS content based on the regulatory landscape of the states/countries in which the product is sold. In addition, Oeko-Tex certifications²² can be obtained to ensure that products meet the requirements for quality and regulatory compliance throughout the supply chain.

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. Further changes to Oeko-Tex Eco Passport certification will make the previously voluntary self-assessment mandatory for all production sites from April 2023.²³ Debbie Chronicle, senior sales executive, Hohenstein, will discuss the latest developments in her talk entitled “Effective PFAS Testing and Supply Chain Strategy” at the July 11-12, 2023, AATCC Navigating a Path Forward for PFAS in Textiles program.²⁴

PFAS ALTERNATIVES

Research into the use of non-fluorinated PFAS alternatives for textile repellency treatments has been underway for some time.² The ability to impart water repellency to textiles using these alternatives is now available. Research on extending these performance features with oil repellency is being investigated.^{25,26} Many consumer textile products do not require oil repellency. As these newer treatments are adopted by industry, details may be unavailable, as they are often considered as trade secrets or proprietary.

Scott Efird, principal consulting director, Efird Textile Consulting LLC, stated that “as of today, there is not a commercially available PFAS-free water and oil repellent on the market. There are a couple that claim ‘non-detectable C6 [six-carbon PFAS]’ with oil repellency, but they still use some quantity of C6 to get the oil repellency performance. All major chemical manufacturers have a PFAS-free DWR (durable water repellent), and many are bio-based or partially bio-based. From my experience, the performance is good, but is slightly less than C6 chemistry.”

One example of a PFAS-free DWR treatment is Chemours Teflon EcoElite finish. It is bio-based and renewably sourced, durable, and does not impair fabric breathability.²⁷

Another example comes from Rudolf GmbH, who market a line of DWR treatments for the textile industry.²⁸ Luka Stefan Kovacevic, Senior Technical and Business Development Manager for Rudolf, says that “the demand for these alternatives in industry [are] rapidly growing.” These include dendrimers, acrylics, urethanes, and others to replace PFAS in repellent finishes. Kovacevic will be speaking at the AATCC July 2023 PFAS program.²⁴

Alternatives to PFAS chemistry that have **both** repellency features are now being sought. Researchers at the University of Toronto have reported achieving this dual repellency using suitable fabric constructions and silicones.^{25,26} Similar work was done by a group at Soochow University on rough surface synthetic fabric treated with chlorosilane to create silanol-coated fabric.²⁹ In February 2023, AGC Chemicals Americas Inc. and Dryfiber LLC announced that they are jointly developing a commercial new non-fluorinated oil/water repellent technology that imparts a rough texture to the fabric surface.³⁰ Fabric surface roughness and surface energy are major factors contributing to superoleophobicity (oil repellency).³¹

Kovacevic states, however, that oil repellency will be difficult to achieve with non-fluorinated alternative treatments. “Our experience shows that, and [on] this we agree with many other manufacturers of fluorinated and non-fluorinated chemistry, only fluorine chemistry can provide oil repellency because it’s a physical chemical property that this class of chemicals incorporates,” says Kovacevic.

However, the search goes on as regulatory agencies and environmental groups continue to press for a total ban on PFAS. “C6 fluorocarbon chemistry was supposedly better [as compared to C8] in terms of its toxicological profile... is less bio-accumulative,” says Kovacevic. But “the carbon-fluorine bond is one of the strongest chemical bonds known. Once produced, it will last forever in the environment. Do we really need to have this kind of chemistry in everyday items?”

Therefore, emphasis may be placed on limiting C6 use to personal protective equipment (PPE), according to Kovacevic, “where you need chemical and oil resistance or repellency, on medical textiles where you need blood repellency..., high visibility clothing, and military apparel.”

Solutions

Due to the complexity of the regulatory environment, both in the US and the EU, consulting services have become available to aid industry in determining what alternatives are practical on a case-by-case basis. A group at RTI International in Research Triangle Park, NC, USA, RTI Innovation Advisors, are available to help textile manufacturers make decisions on what non-fluorinated alternatives are suitable for meeting performance and regulatory requirements applicable in their state or country.³²

“The best solution to a problem is not going to necessarily be one that’s right in front of your face. When we have clients come to us and say, ‘here’s this issue I’m running into,’ we like to cast a wide net to identify solutions and not just look within their own relevant industry. When it comes addressing PFAS in textiles, it’s important to not just look within the obvious avenues, but [to] expand outside of that by investigating adjacent and niche industries and what types of solutions they’re working on,” says Kayla Messier Jones, innovation analyst at RTI International.

“We have various clients who are stakeholders within the textile industry...we’ve worked with and supported AFFOA [Advanced Functional Fabrics of America]³³ on several occasions...we’re also currently working under a grant with NC DMCSPP [North Carolina Defense Manufacturing Community Support Program]³⁴ to support innovation around advanced textiles, and wearables to support the war fighter, so we’re very involved in that work along with the North Carolina State Wilson College of Textiles³⁵ and a number of other fantastic organizations,” says Jones. “We also work with brands supplying textile-based products to consumers...we’re excited to do more to support innovation within the textile industry.”

WHAT’S NEXT?

Adapting to the rapidly changing regulatory environment worldwide is a major challenge. The textile industry is striving to keep up and explore economically feasible alternatives to PFAS use. Performance of the final treated product should include protective ability, breathability, good washfastness, and overall durability. There is no one-size-fits-all solution manufacturers can rely on. What’s needed is the application of creative scientific and manufacturing practices in textile production to lead us to a more sustainable future.



These issues and more will be explored at the July 11-12, 2023, AATCC Navigating a Path Forward for PFAS in Textiles program.²⁴ Join in and contribute to this important discussion.

www.aatcc.org/aatcc-events/pfas2023

References

1. https://web.archive.org/web/20120217011800/http://www2.dupont.com/Heritage/en_US/1938_dupont/1938_indepth.html (accessed April 2023)
2. https://pfas-1.itrcweb.org/wp-content/uploads/2022/09/HistoryandUse_PFAS_Fact-Sheet_090722_508.pdf (accessed April 2023)
3. <https://pfasproject.com/parkersburg-west-virginia/> (accessed April 2023)
4. <https://comptox.epa.gov/dashboard/chemical-lists/PFASMASTER> (accessed April 2023)
5. <https://www.epa.gov/sdwa/drinking-water-health-advisories-genx-chemicals-and-pfbs> (accessed April 2023)
6. Cousins, I. T.; Johansson, J. H.; Salter, M. E.; Sha, B.; and Scheringer, M. Outside the Safe Operating Space of a New Planetary Boundary for Per- and Polyfluoroalkyl Substances (PFAS). *Environ. Sci. Technol.* **2022**, *56*, 11172–11179. DOI:10.1021/acs.est.2c02765
7. <https://www.nrdc.org/resources/review-pfas-chemical-class-textile-sector> (accessed April 2023)
8. <https://www.textileworld.com/textile-world/features/2021/05/dyeing-printing-finishing-pfas-a-textile-perspective/> (accessed April 2023)
9. <https://www.cattermoleconsulting.com/pfas-regulations-are-increasing-in-many-u-s-states/> (accessed April 2023)
10. <https://newsroom.astm.org/newsroom-articles/new-astm-international-efforts-will-focus-chemical-substances-consumer-products> (accessed April 2023)
11. <https://www.astm.org/e3302-22.html> (accessed April 2023)
12. <https://www.epa.gov/eg/current-effluent-guidelines-program-plan> (accessed April 2023)
13. <https://www.epa.gov/system/files/documents/2023-01/ELG%20Plan%2015%20Fact%20Sheet.pdf> (accessed April 2023)
14. https://www.epa.gov/system/files/documents/2023-01/11143_ELG%20Plan%2015_508.pdf (accessed April 2023)
15. Rexhepi, D. Chemical Applications Interest Group Meeting, AATCC, Research Triangle Park, NC, USA, March 30, 2023.
16. <https://www.epa.gov/cwa-methods/cwa-analytical-methods-and-polyfluorinated-alkyl-substances-pfas#draft-method-1633> (accessed April 2023)
17. <https://www.epa.gov/cwa-methods/cwa-analytical-methods-and-polyfluorinated-alkyl-substances-pfas#draft-method-1621> (accessed April 2023)
18. <https://www.epa.gov/sdwa/and-polyfluoroalkyl-substances-pfas> (accessed April 2023)
19. <https://echa.europa.eu/-/echa-publishes-pfas-restriction-proposal> (accessed April 2023)
20. Cousins, I. T.; Goldenman, G.; Herzke, D.; Lohmann, R.; Miller, M.; Ng, C. A.; Patton, S.; Scheringer, M.; Trier, X.; Vierke, L.; Wang, Z.; and DeWitt, J. C. The concept of essential use for determining when uses of PFASs can be phased out. *Environ. Sci.: Processes Impacts* **2019**, *21*, 1803–1815. DOI: 10.1039/C9EM00163H
21. <https://www.hohenstein.us/en-us/> (accessed April 2023)
22. <https://www.hohenstein.us/en-us/oeko-tex> (accessed April 2023)
23. <https://www.oeko-tex.com/en/news/press-releases/oeko-tex-new-regulations-2023/press> (accessed April 2023)
24. <https://www.aatcc.org/aatcc-events/pfas2023/> (accessed April 2023)
25. <https://sustainabilitycommunity.springernature.com/posts/finally-oil-repellent-textiles-that-do-not-utilized-perfluorinated-compounds> (accessed April 2023)
26. Shabanian, S.; Khatir, B.; Nisar, A.; and Golovin, K. Rational design of perfluorocarbon-free oleophobic textiles. *Nat. Sustain.* **2020**, *3*, 1059–1066. DOI:10.1038/s41893-020-0591-9
27. <https://www.teflon.com/en/industries-and-solutions/solutions/consumer-applications/textile-finishes/how-ecoeelite-works> (accessed April 2023)
28. <https://rudolf.de/> (accessed April 2023)
29. Jiang, L.; Cheng, Y.; Wang, S.; Xu, Z.; and Zhao, Y. Non-Fluorine Oil Repellency: How Low the Intrinsic Wetting Threshold Can Be for Roughness-Induced Contact Angle Amplification? *Langmuir* **2022**, *38* (18), 5857–5864. DOI:10.1021/acs.langmuir.2c00478
30. <https://www.agcchem.com/news/2023/february-9-2023-agc-chemicals-and-dryfiber/> (accessed April 2023)
31. Kota, A. K.; Mabry, J. M.; and Tuteja, A. Superoleophobic surfaces: design criteria and recent studies. *Surface Innovations* **2013**, *1* (2), 71–83. DOI: 10.1680/si.12.00017
32. <https://www.rti.org/impact/replacing-polyfluoroalkyl-substances-with-safer-chemicals> (accessed April 2023)
33. <https://affoa.org/> (accessed April 2023)
34. <https://www.ies.ncsu.edu/defense-industry-initiatives/dmcspp/> (accessed April 2023)
35. <https://textiles.ncsu.edu/> (accessed April 2023)

J. Michael Quante is a science editor, retired in 2021 from AATCC. He was primarily responsible for editing peer-reviewed articles for the *AATCC Journal of Research*. His current interests are writing about industrial uses of new technologies, potential applications of emergent research, sustainability, and biomimicry. www.linkedin.com/in/mikequante

Disclaimer: Responsibility for opinions expressed in this article is that of the author and quoted persons, not of AATCC. Mention of any trade name or proprietary product in AATCC Review does not constitute a guarantee or warranty of the product by AATCC and does not imply its approval to the exclusion of other products that may also be suitable.