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Durable Water and Soil repellent chemistry in the textile industry – a research report

P05 Water Repellency Project

Contents

Executive Summary

Durable water repellents (DWRs) are topical finishes applied to fabrics to provide protection against water, oil and soil. DWR finishes add value to textile products. In addition to providing protection against water, oil and soil, these finishes also extend the life of products and keep them looking newer longer. DWR technology has historically been achieved with textile finishes that contain a polymer to which long-chain perfluoroalkyl groups have been attached. These long-chain fluorinated polymers often contain residual raw materials and trace levels of long-chain perfluoroalkyl acids (PFAAs) as impurities. The residual raw materials and the product themselves may degrade in the environment to form long-chain PFAAs.

In 2011, the ZDHC brands made a commitment to set forth a timeline for the elimination of DWR technologies which may contain or degrade into long-chain PFAAs such as PFOA and PFOS. The ZDHC brands have collaborated with the Outdoor Industry Association (OIA), the European Outdoor Group (EOG), and representatives from the chemical industry to understand opportunities, challenges and limitations for eliminating DWR technologies associated with long-chain PFAAs. The ZDHC brands reached out to chemical manufacturers, industry associations, regulatory agencies and other organizations for information on commercially available alternative short-chain and non-fluorinated DWR technologies and chemistries. An online search for alternative DWR technologies and chemistries for textile applications was also conducted. The ZDHC brands developed a categorization table for the different types of fabrics and their performance requirements and hazard criteria to evaluate the alternative DWRs.

Since the 1950's, long-chain PFAAs as well as polymers and surfactants containing long-chain perfluoroalkyl functionality that may degrade to form long-chain PFAAs have been widely used in numerous industries and commercial applications. As a result of the widespread uses, long-chain PFAAs including PFOA and PFOS have been detected globally in the environment, wildlife and humans. PFOA and PFOS, the most widely known and studied long-chain PFAAs, have been shown to be persistent in the environment, have long elimination half-life in wildlife and humans, and have toxicological properties of concern. Due to these properties, regulatory actions have been put in place or are being considered in several countries to manage these substances. There is also a shift within industries towards DWR chemistries containing shorter perfluoroalkyl chains as well as non-fluorinated chemistries.

Short-chain fluorinated chemistries are promoted as having favorable health and environmental properties. They are known to be less toxic and have low bioaccumulative potential. They are, nonetheless, associated with substances that may be of concern particularly in cases where their use can result in widespread dispersion in aquatic environments. Short-chain fluorinated DWR finishes cannot break down in the environment into PFOA and PFOS. Like fluorinated chemistries, non-fluorinated chemistries are also associated with substances of concern. For example, stearic acid-melamine chemistry releases formaldehyde, a known human carcinogen. Wastewater

from the residual bath of silicone finishes application processes is toxic to fish. Additionally, evidence suggests that nano-based chemistries may have toxic properties to both human health and the environment and may have greater risk than larger particle.

Performance of DWR finishes is a complex property to evaluate since performance is based on several fabric attributes. It is dependent on the end use of the textile product, the fabric type, fabric breathability, finishes resistance to repeated home laundering, dry cleaning and abrasion etc. In addition, there is not a clear correlation between the myriad fabric attributes provided by DWR finishes. Some DWR finishes are better at certain performance effects than others and there is the possibility that the level of performance of one effect may be negatively affected by lack of other effects in certain cases. In assessing the performance level of DWR finishes, test methods by AATCC, ISO and ASTM are the most widely employed. There is currently no “industry standard” performance level for DWR finishes on textile products. Performance levels and practical methods for assessing performance are set by individual brands and retailers based on their understanding of consumer demands for a garment during its use. Hence there are significant variations in performance testing regimes and these testing regimes often constitute brands’ intellectual property.

Online searches for short-chain fluorinated DWR chemistries using scientific journals yielded no results. Information about short-chain fluorinated chemistries was only available through chemical manufacturers. There were a limited number of chemical manufacturers who responded to the request for information on commercially available alternative DWR technologies and chemistries. Information about commercially available alternative DWR finishes containing short-chain fluorinated chemistries received from the chemical producers contacted was predominantly DWR finishes product brochures. These DWR finishes claim to offer comparable or superior performance attributes associated with finishes containing long-chain fluorinated chemistries. Very limited information was provided regarding performance levels, methods used to evaluate the performance of these short-chain fluorinated chemistries.

With respect to potential health and environmental impacts, few hazard data was provided by chemical manufacturers for the DWR finishes containing short-chain chemistries. Some short-chain fluorinated chemistries claim they do not break down in the environment into PFOA and PFOS. Others claim to be PFOA- and/or PFOS-free, explaining that these chemicals may be present as impurities but below their levels of detection.

Information on commercially available non-fluorinated chemistries made available by chemical manufacturers included the acrylic- and urethane-based, as well as other conventional chemistries such as paraffin, silicone and stearic acid-melamine. These commercially available non-fluorinated chemistries only claim to provide water repellency. No non-fluorinated chemistry is marketed as a stain release finish. Similar to the short-chain fluorinated chemistries, there was limited information provided on the performance of these non-fluorinated chemistries.

Moving from long chain to short-chain fluorinated DWR chemistries is a complex process that requires in-depth research in order to realize opportunities that exist and to make an informed decision about when a move to short-chain fluorinated DWR chemistries can occur. Future research projects on this subject should consider, among other practical steps for moving from long-chain fluorinated chemistries, the overall risk and socio-economic impact associated with short-chain fluorinated chemistries

The move from fluorinated to non-fluorinated DWR chemistries is much more challenging and one that also require in-depth research to realize the practical application of non-fluorinated DWR finishes on textile products. Research and development efforts are also needed to make certain that non-fluorinated chemistries can provide the desired fabric attributes as well as meet their defined performance requirements. Presently, commercially available non-fluorinated chemistries do not provide oil repellent and stain release attributes on fabrics. These attributes, in addition to several others, are demanded for certain product groups by their end users.

List of key terms and definitions

C4 – a technology or chemistry based on perfluoroalkyl chains with four fluorinated carbons (e.g., C_4F_9-).

C6 – a technology or chemistry based on perfluoroalkyl chains with six fluorinated carbons (e.g., C_6F_{13}-).

C8 – technology or chemistry based on perfluoroalkyl chains with eight or more fluorinated carbons (e.g., C_8F_{17}-).

Durable water repellent (DWR) – a textile finish whose performance attributes (effects) may include water repellency, oil repellency, stain repellency, soil repellency, stain release, soil release, and durability (e.g. to laundering, dry cleaning, abrasion, light exposure, rain, etc.)

Fluorinated polymer – a general term used to describe a polymer which has a hydrocarbon backbone (polyamide, polyester, polyurethane, etc.) to which is appended a fluorinated carbon chain, also known as a fluorinated alkyl chain or fluoroalkyl chain.

Fluorocarbon – an organic compound that contains fluorine.

Fluorochemical – a general term used to describe broadly all chemicals containing the element fluorine, used synonymously with fluorinated chemical.

Fluoropolymer – a fluorinated polymer made by (co) polymerization of monomers that contain fluorine to create a polymer with fluorine directly bound to carbons of the polymer backbone.

Homologues – one of a series of compounds, each of which has a structure differing regularly by some increment (number of carbons) from adjacent members of the group.

Long-chain perfluoroalkyl acids – PFCAs with perfluoroalkyl chains lengths C8 and higher, including PFOA; PFSA with carbon chain lengths C6 and higher, including PFHxS and PFOS. (Long-chain as defined by OECD (http://www.oecd.org/ehs/pfc/)

Perfluorinated chemicals – chemicals in which all carbon-hydrogen bonds in a chain have been replaced by carbon-fluorine bonds. Examples include PFOA and perfluorooctane sulfonate PFOS.

Perfluoroalkyl/perfluorinated chain – a chain of carbon atoms where all hydrogen has been replaced with fluorine (e.g., C_nF_{2+1}- where n >1).

Perfluoroalkyl acids (PFAAs) – describes the family of chemicals including PFOS and PFOA. These are perfluorinated compounds in which all hydrogen atoms on the carbon chain have been replaced with fluorine atoms and which have a functional acid group at the terminus of the perfluoroalkyl chain.

Perfluoroalkyl carboxylic acid (PFCA) – a generic term used to describe any perfluorinated carbon chain length carboxylic acid, including higher and lower homologues as well as PFOA.

Perfluoroalkyl sulfonate (PFSA) – a generic term used to describe any fully fluorinated carbon chain length sulfonic acid, including higher and lower homologues as well as PFOS.

Perfluorobutane sulfonic acid (PFBS, $C_4F_9SO_3H$ or $CF_3CF_2CF_2CF_2SO_3H$) – a chemical containing a four carbon perfluoroalkyl chain attached to a sulfonic acid functional group.

Perfluorocarbon – a chemical substance that is comprised of only carbon and fluorine.

Perfluorohexanoic acid (PFHxA, $C_5F_{11}CO_2H$) – a chemical containing a five carbon perfluoroalkyl chain attached to a carboxylic acid functional group.

Perfluorohexane sulfonate (PFHxS, $C_6F_{13}SO_3H$) – a chemical containing a six carbon perfluoroalkyl chain attached to a sulfonic acid functional group.

Perfluorooctanoic acid (PFOA, $C_7F_{15}CO_2H$) – a chemical containing a seven carbon perfluoroalkyl chain attached to a carboxylic acid functional group.

Perfluorooctane sulfonate (PFOS, $C_8F_{17}SO_3H$) – a chemical containing an eight seven carbon perfluoroalkyl chain attached to a sulfonic acid functional group.

Precursor – a chemical that can be transformed to produce another chemical.

Short-chain perfluoroalkyl acids – PFCAs with carbon chain lengths C7 and lower, including PFHxA and PFSAs with carbon chain lengths C5 and lower, including PFBS.

1. Introduction

1.1 Background

Durable water repellent (DWR) technology has historically been achieved with textile finishes that contain a polymer to which long-chain perfluoroalkyl groups have been attached or non-fluorinated finishes. Long-chain fluorinated polymers often contain residual raw materials and trace levels of long-chain perfluoroalkyl acids (PFAAs) as impurities. The residual raw materials and the product themselves may degrade in the environment to form long-chain perfluoroalkyl acids.

In 2011, the ZDHC brands made a commitment to set forth a timeline for the elimination of DWR technologies which may contain or degrade into long-chain PFAAs such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS). The ZDHC brands has collaborated with the Outdoor Industry Association (OIA), the European Outdoor Group (EOG), and representatives from the chemical industry to understand the opportunities, challenges and limitations for eliminating DWR technologies associated with long-chain PFAAs.

1.2 Purpose and scope

The purpose of this report is to compile and summarize information about commercially available alternative DWR technologies and chemistries and describe the steps involved in moving from long-chain to short-chain and non-fluorinated technologies and chemistries. The primary focus of the report is on DWR technologies and chemistries with short-chain fluorinated chemistries for textile applications. This report characterizes the various types of repellent chemistries (both fluorinated and non-fluorinated), their performance attributes and limitations, and their related human health and environmental properties. It briefly describes repellent finishing processes, textile fabric performance attributes and how performance is evaluated.

This report also presents information from chemical producers and industry associations about commercially available alternative DWR technologies and chemistries. In order to determine the feasibility of the alternative technologies and chemistries, performance (for both priority and general products) and hazard criteria need to be defined to evaluate the alternatives. The performance criteria would include water and oil repellency, stain release as well as other important performance attributes such as fabric breathability, durability, etc. The hazard criteria would be used to evaluate the potential human health and environmental impacts associated with the alternative technologies and chemistries. Similar to performance, specific human health and environmental endpoints would be defined. These endpoints would include acute and chronic mammalian and aquatic toxicities, environmental persistence and bioaccumulation. Additionally, chemistries recognized to be of high concern by national and international regulatory bodies would be identified. For each alternative DWR technology and chemistry, chemical specific information would be documented. An attempt would be made to identify the composition of chemical mixtures and their byproducts.

Lastly, this report would provide recommendations in moving from DWR technologies and chemistries containing long-chain perfluoroalkyl functionality to technologies and chemistries containing short-chain perfluoroalkyl functionality. This would include factors to be addressed in making a technology or chemical substitution.

2. Research methodology

Two primary strategies were utilized to identify commercially available alternative DWRs with short-chain and non-fluorinated technologies and chemistries. They were outreach to organizations and an online research.

2.1 Outreach to organizations

The following steps were carried out to outreach to chemical manufacturers including manufacturers of long-chain fluorinated chemistries and other organizations:

1. Developed list of major chemical producers (such as Huntsman, DuPont, Clariant, Dystar, BASF, etc.); chemical and apparel/footwear industry associations; research institutes; national and international chemical regulatory agencies (Danish EPA, US EPA, UNEP, etc.); apparel/footwear brands; and non-clothing companies that may employ or have information on water, oil or stain repellent technologies and/or chemistries.
2. Reviewed the respective websites of the chemical producers, industry associations, regulatory agencies and the other companies to determine whether or not they produce or have information on alternative DWR technologies and chemistries.
3. Created a master list of the companies and organizations to contact for information on alternative DWR technologies and chemistries.
4. Drafted and submitted an email to the contacts on this list requesting information about short-chain and non-fluorinated alternative DWR technologies and chemistries.
5. Documented all the information received in a in a single location. Information to document included chemical manufacturer, technology or chemistry, process description, performance, health and environmental hazards, etc.

2.2 Online research

The second strategy involved an online search for alternative DWR technologies and chemistries using key terms. Examples of key terms included *short-chain fluorinated water repellent, alternatives to long-chain fluorinated DWR, alternatives to PFOA and PFOS water repellents, short-chain fluorinated DWR* and *durable water repellents*. Online sources used to conduct research included scientific journals and online search engines, such as *Google* and *Google scholar*.

ScienceDirect and *Wiley InterScience* journal databases contain series of scientific journals that were reviewed for articles on DWR technologies and chemistries. The following are other scientific journals that were reviewed:

- *Journal of Industrial Textiles*
- *Journal of the Textile Institute*
- *Textile Research Journal*
- *Journal of Material Chemistry*
- *Journal of Applied Polymer Science*
- *Advance Functional Materials*
- *Journal of Colloid and Interface Science*

In conducting the online search for alternative DWR technologies and chemistries, the procedures listed below were followed.

a. Obtained access to the journals listed above if subscription is not free.
b. Searched journal databases using key terms to identify articles on alternative technologies and chemistries.

2.3 Evaluation of alternative DWR technologies and chemistries

The identified alternative (short-chain and non-fluorinated) DWR technologies and chemistries would be evaluated on their performance and health and environmental attributes to establish a list of potentially feasible technologies and chemistries. Preliminary criteria were developed to evaluate the alternative DWR technologies and chemistries proposed by companies, institutions and/or agencies for performance feasibility. The criteria indicated minimum performance levels that can be used to screen-out less suitable technologies and chemistries with respect to water and oil repellency, stain release, fabric breathability, durability, etc. Experts and stakeholders provided input in determining the elements included in performance level criteria. Additional research (including an online research) was required if the information provided on the alternative DWR technologies and chemistries to aid in performance evaluation is incomplete.

Criteria used to assess the human health and environmental hazards of the alternative DWR technologies and chemistries were also developed. Again, inputs from experts were used to determine the hazard criteria. Additional research to identify potential hazards of the DWR technologies and chemistries was also required if information provided is incomplete. With respect to human health and environmental effects, any applicable national and international regulation that exists on the alternative technologies and chemistries were included.

3. Overview of durable water repellent finishes

Durable water repellents (DWRs) are topical finishes applied to fabrics to provide protection against water, oil and soil. DWR finishes add value to textile products. In addition to providing protection against water, oil and soil, these finishes also extend the life of products and keep them looking newer longer.[1] DWR finishes are applied at varying amounts to achieve a specific level of performance which is set by a brand or retailer selling the finished textile product.

The DWR is a polymer, in particle form, that has pendant fluoroalkyl chains attached to the polymer backbone. On the fabric surface, the polymer particle melts and spreads to cover the fabric surface during the drying of the fabric after it has been applied. The fluoroalkyl chains orient perpendicular to the fabric surface. It can be imagined as microscopic umbrellas connected to the polymer backbone. This myriad of “umbrellas” creates a low surface energy surface on the fabric. The surface energy is lower than water or oils. Therefore, when water or oils contact the fabric surface they cannot wet or spread out, they bead up having a high "contact angle." An optimized DWR finish is designed for a specific fabric based on its fiber type and fabric construction to form an array of microscopic polymer domains on the fabric surface (not a film or coating) with the fluorinated chains erect, perpendicular to the fabric surface and close enough to one another to act like a continuous surface. The image is a plethora of microscopic umbrellas on the surface with the tips touching so that no water or oil can penetrate to the fabric. Water or oil cannot spread out, forcing them to bead up and slide off the fabric.[2]

At present, there is not a single acceptable performance level for DWR finishes on apparel. The required performance level of the DWR finish is dependent on the apparel products, their intended uses and other important factors such as their durability to laundering and dry cleaning, resistance to abrasion and fabric breathability. While relatively lower performing finishes may be suitable for certain consumer products, other products necessitate high performing DWR finishes. For example, a high performance rain jacket may require a different DWR performance than a shirt intended for casual use. Likewise, apparel which is frequently laundered requires a different level of performance than one which is not.

Water repellency can be achieved with many types of finishes, including waxes, oils and silicones but these compounds can be penetrated by oil, including lotions and oils from skin. The most effective or high performing DWR finishes are those containing perfluoroalkyl functionalities. As such, fluorinated chemistries have been the most widely used DWR finishes for textile applications as they are the most effective at repelling both oil and water. They can be applied to both natural and synthetic fibers and their blends, and meet performance specifications over a wide range of requirements.[3]

Fluorinated chemistry works by binding and fixing the fluorinated polymer to the fiber surface in such a way that it remains fixed even after many washings. The repellency finish allows; liquids to bead up and roll off the fabric, liquid spills to be easily wiped away when blotted with a clean cloth and dry soil can be brushed off easily.

Non-fluorinated chemistries are also used as DWR for textile products. These include paraffin, stearic acid-melamine and silicone chemistries, as well as chemistries containing dendrimers and nano-materials.[4,5]

4. Repellent chemistries for textile applications

4.1 Long-chain fluorinated repellent chemistries

Historically, DWR containing long perfluoroalkyl chains have been the chemistry of choice for textile applications. Perfluorinated chemicals are used to incorporate raw materials containing a perfluoroalkyl chain into acrylic or urethane polymer that are used as DWR finishes. When applied to fabrics, these finishes form a structure on the outer surface of fiber to provide maximum repellency. The unique water and oil repellency properties of DWR finishes are derived from the perfluoroalkyl chain that is attached to the acrylic or urethane polymer backbone.

DWR finishes containing long-chain perfluoroalkyl functionality are modified to have a wide range of properties to fit the different demands of the users and the intended purpose. They allow reduction in volume of the finishes that can be applied and consequently reducing associated costs and life-cycle impacts for a treated garment.[6,7] They also have excellent chemical and thermal stability which provides treated fabrics with good durability (e.g., during laundering and dry-cleaning.[8] Most repellents based on this chemistry are applied by padding process and then dried and cured.[9]

4.1.1 Concerns of long-chain perfluoroalkyl acids

Since the 1950's long-chain PFAAs as well as polymer and surfactants containing long-chain perfluoroalkyl functionality (termed by some as "C8") that may degrade to form long-chain PFAAs have been widely used in numerous industrial and commercial applications.[10,11] As a consequence of this widespread use, long-chain PFAAs including perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) have been detected globally in the environment, wildlife and humans.

Concerns about the potential environmental and human health impacts of these long-chain PFAAs have led to actions by regulators and industry. Long-chain PFAAs have been defined as (i) perfluorocarboxylic acid (PFCA) and perfluoroalkyl sulfonates (PFSA) with a minimum of 8 and 6 carbon chain lengths, respectively and (ii) substances, such as fluorinated polymers that may break down to form long-chain PFAAs.[12,13] The PFCA subcategory of long-chain PFAAs includes PFOA, higher homologues, and their salts and precursors. The PFSA subcategory includes perfluorohexane sulfonic acid (PFHxS), PFOS, higher homologues, and their salts and precursors (see Figure 1 below).

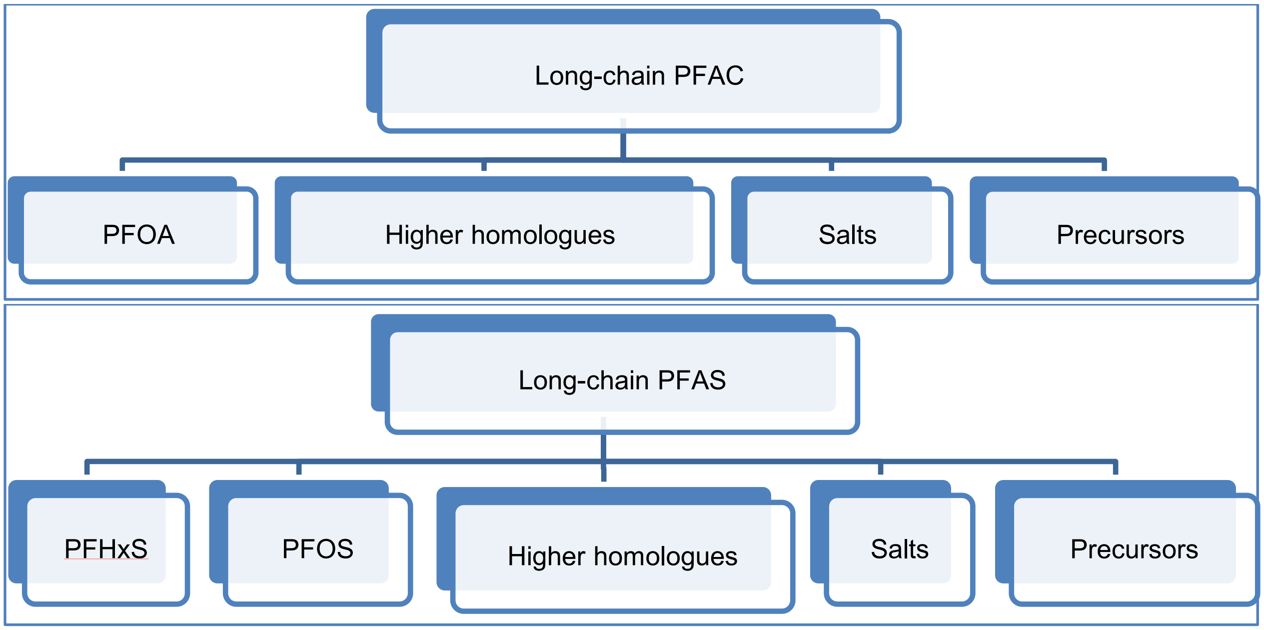

Figure 1: Categories and subcategories of long-chain perfluoroalkyl acids (PFAAs)[14]

Source: United States Environmental Protection Agency (U.S.EPA)

Over time, DWR finishes with the long-chain chemistries on textiles can wear off. Intensive washing of textiles increases the amounts of the finishes that are lost to the environment.[15] In the course of their intentional use in products or unintended loss, long-chain PFAAs are released into the environment in significant quantities. PFOA and PFOS are the most widely known and studied of the long-chain PFAAs.[16]

As a result of their strong carbon-fluorine bonds, PFOA and PFOS do not break down in the environment. They have been shown to be persistent in the environment and have long elimination half-life in wildlife and in humans. Numerous reports have documented the presence of long-chain PFAAs in aquatic environments in Japan, United States, Germany and Italy, with PFOA and PFOS comprising the most detected chemicals.[17,18] It should be noted that PFOA and PFOS can also be unintentionally produced. For example, PFOA can be produced by degradation of other fluorinated chemicals.[19] It can be found in consumer products as an impurity and unintended byproduct, and not as a deliberately added ingredient. This is particularly the case in products treated with perfluoroalkyl-containing chemicals.[20] In ecosystems and in living organisms, chemicals such as perfluorosulfonamide can be biotransformed to PFOS.[21]

Since PFOA and PFOS are ubiquitous in the environment, exposure to these chemicals is also widespread. PFOS was the predominant perfluorinated chemical found among

473 human blood samples collected from United States, Colombia, Brazil, Belgium, Italy, Poland, India, Malaysia, and Korea.[22] Other detected perfluorinated chemicals in the blood samples included PFOA. In the United States, PFOA and PFOS were detected in over 98 percent of 2,094 serum samples collected between 2003 and 2004.[23] Breast milk samples collected from mothers from Sweden and China have also been found to contain PFOA and PFOS.[24,25] To date, epidemiologic data is insufficient to conclusively associate these chemicals with any of the diseases of concern.[26] Nonetheless, toxicological studies and the limited epidemiologic studies have associated PFOA and PFOS to severe adverse health outcomes, including reproductive and developmental effects, immune system effects and cancer.[27]

4.1.2 Regulatory and industry initiatives on long-chain perfluoroalkyl acids

Given the persistent, bioaccumulative and potentially toxic nature of long-chain PFAAs, regulatory actions have been put in place or are being considered in several countries to manage them.[28]

Canada has added PFOS to its Virtual Elimination List of toxic substances, prohibiting the manufacture, use and sale of PFOS or products containing PFOS.[29] The European Commission's Scientific Committee on Health and Environmental Risks (SCHER) has classified PFOS as very persistent, very bioaccumulative and toxic, and its use is restricted in the European Union (EU).[30] The Commission is also considering similar restriction for PFOA since its health and environmental risk profile is comparable to PFOS.

In 2009, the Stockholm Convention added PFOS to its list of persistent organic pollutants (POPs).[31] PFOS and PFOS-related substances in firefighting foams and textiles have been banned in Norway since 2007.[32]

The United States Environmental Protection Agency (U.S.EPA) is considering initiating section 6 rulemaking of the Toxics Substances Control Act (TSCA) to manage long-chain PFAAs. The TSCA section 6 provides U.S.EPA with the authority to ban or restrict the manufacture, processing or use of these chemicals.[33]

The Australian National Industrial Chemicals Notification and Assessment Scheme (NICNAS) has recommended restricting uses of PFOS, except for essential uses for which no suitable or less hazardous alternatives are available.[34]

There are also voluntary initiatives aimed at reducing the uses of long-chain PFAAs. Under the U.S.EPA PFOA Stewardship Program, eight major manufacturers of PFOA have committed to phasing out PFOA by the end of 2015.[35] In 2000, 3M – one of the major manufacturers of PFOA and PFOS– decided to phase out production of PFOS and PFOS-related products and has developed a new technology to reformulate products that are affected by the phase out.[36]

4.2 Other repellent chemistries for textile applications

4.2.1 Short-chain fluorinated repellent chemistries

In light of the concerns associated with long-chain PFAAs, there is a shift towards DWR chemistries with shorter perfluoroalkyl chains (also termed “C6” or C4” depending on the number of carbons in the perfluoroalkyl chain). Chemically, short-chain fluorinated chemistries are closely related to their long-chains homologues. DWRs containing short-chain fluorinated chemistries are produced using perfluoroalkyl raw materials such as fluorotelomer alcohols that are not expected to break down in the environment into PFOA and PFOS.[37]

Short-chain fluorinated DWR chemistries are now promoted by the chemical industry as having comparable repellency and other performance attributes to long-chain chemistries. The industry is, in fact, on a learning curve to match the performance levels of DWR finishes with long-chain fluorinated chemistries. In general, short-chain fluorinated DWR chemistries are not as effective as those with long-chain chemistries, particularly in repelling oil. For higher performance applications including 50 or more home laundering cycles, and strong rain and aggressive stain resistance, there are reductions in performance levels achieved with short-chain fluorinated DWR chemistries. Although certain performance levels may eventually be achieved, it is understood that there are critical applications where the required performance levels may never be achieved by short-chain fluorinated DWR chemistries.

In less critical applications, the reduced performance levels of short-chain fluorinated DWR chemistries can be compensated by applying higher amounts of finishes. The claim that short-chain fluorinated chemistries are substitutes for DWR finishes with long-chain chemistries may not necessarily imply a simple replacement of currently used DWR finishes. Substituting a long-chain with short-chain fluorinated DWR chemistries may require optimizing application methods.

Although short-chain fluorinated DWR chemistries cannot break down in the environment into PFOA and PFOS, degradation by-products of short-chain fluorinated chemistries may also be substances of concern. Potential byproducts of the short short-chain fluorinated chemistries include perfluorohexanoic acid (PFHxA) and perfluorobutane sulfonic acid (PFBS). Both of these substances are persistent in the environment. They are, nonetheless, recognized to be less toxic and bioaccumulative according to available studies.[38] Given that substances associated with short-chain fluorinated chemistries are persistent in the environment, uses which may cause widespread dispersion run the risk of not being approved for use in certain countries. For example, the Australian government has taken measures to restrict any use of PFBS-based substances that would result in widespread dispersion in aquatic environments.[39]

4.2.2 Paraffin repellent chemistries

Paraffin was one of the earliest water repellent chemistries used. These repellent products are generally emulsions containing aluminum or zirconium salts of fatty acids, usually stearic acid. They provide good water repellency due to their zirconium ion holding onto fiber, and the fact that their water repellent groups have good orientation on fiber surfaces. They are generally compatible with other types of textile finishes but they have increased flammability. Despite providing good water repellency effects, paraffin repellents do not repel oil and are generally not durable to laundering and dry cleaning. Additionally, fabrics treated with paraffin-based finishes are less permeable by air and vapor, resulting in poor wear comfort. Paraffin repellent finishes can be applied by both padding and exhaustion finishing processes.[40]

4.2.3 Stearic acid-melamine repellent chemistries

Stearic acid-melamine repellent chemistries are composed of compounds formed by a reaction between stearic acid and formaldehyde and melamine. The low water affinity characteristic of the stearic acid groups of the finish provide the water repellency, while the N-methylol groups that are formed react with cellulose or with each other to generate permanent repellent effects.

An advantage of stearic acid-melamine repellents is that they have increased durability to laundering. However, these repellents have decreased abrasion resistance and fabric tear strength, cause changes in the shade of dyed fabrics and release formaldehyde.[41] The release of formaldehyde is a problem for human health and safety given the adverse effects from exposure. Formaldehyde is classified as a known human carcinogen.[42] In facilities where formaldehyde is used or may be potentially released, worker health must be monitored. Formaldehyde is subjected to restriction by regulatory agencies in most industrialized countries, with the concentration allowed in workplace air space limited to 0.1 ppm.[43]

Stearic acid-melamine repellents can be effectively applied to fabrics by exhaustion finishing process but the common application process used is padding. These repellents are in some cases used as extenders for fluorinated DWR chemistries to improve their performance and reduce the amount of fluorochemical used.[44]

4.2.4 Silicone repellent chemistries

Polydimethylsiloxanes are the most common silicone repellents. Their unique structure provides the ability to form hydrogen bonds with fibers and exhibit repellency effects on the outer surface of fibers.

Silicone repellents designed to be durable finishes generally consist of a silanol, a silane and a catalyst such as tin octoate. The silanol and silane components react to form a three-dimensional cross-linked sheath around fibers and the catalyst promotes alignment of the silicone film on the fiber surface, with the outward positioned methyl groups of the silicone polymer generating the water repellency effects.

Silicon repellents offer a high degree of water repellency at relatively low concentrations. Yet, their repellency can be reduced if excess amounts are applied. They have only moderate durability to laundering and dry cleaning, and no oil and soil repellency. Waste water, particularly from residual baths of the finish application processes, is toxic to fish. [45] Some silicone repellents can be applied by exhaustion process (see section 5).

4.2.5 Dendrimer based repellent chemistries

Dendrimer based repellent chemistry is a relatively new field of repellent chemistry. Dendrimers are characterized by regular hyperbranched monomers leading to monodisperse, tree-like structures. The synthesis of monodisperse polymers demands a high level of synthetic control which can be achieved through step by step reaction, building the dendrimer up one monomer layer at a time. The primary components of each dendrimer are the core, internal cavities, branching units and closely packed surface groups.

Historically, dendrimers have been used in the fields of genetics, medicine, biology and chemistry. In textile chemistry, finishes containing dendrimers are applied to fabrics to impart water and oil repellency properties.[46]

4.2.6 Nano-material based repellent chemistries

Repellent chemistries containing nano-materials are coated on fabrics to achieve desirable properties without a significant increase in weight, thickness or stiffness. The properties that can be imparted on textiles using nanotechnology include water repellency and soil resistance. The use of chemistries containing nano-materials to impart water repellency and stain resistance effects on textile is one of the most common ways nanotechnology is being used in the textile industry. To achieve these attributes, fabrics are embedded with tiny fibers, called nano-whiskers. Nano-whiskers form a cushion of air around fiber to repel water and stains. This treatment is believed to be durable to repeated home laundering cycles.[47]

With respect to hazard, there is limited health and safety and environmental impact assessment available of nano-materials. Available evidence suggests that nano-materials have toxic properties to both human health and the environment and may have greater risk than larger particle. Unlike larger particles, nano-materials are capable of being transported within human cells and be taken up by cellular structures and cause cell damage due to their greater chemical reactivity.[48]

5. Repellent finishing processes

Durable water repellent finishes are mostly applied to fabrics after dyeing and/or printing but before the fabrics are made into garments. Other finishes can also be successfully applied to garments. There is not one single process for applying repellent finishes to textile fabrics. The process employed in the finishing largely depends on the chemicals to be used, the fabric type and the available machinery. After finishes are applied to fabrics, they must be dried. In some cases, curing is necessary to achieve the ideal level of performance on finished fabrics. Chemicals with strong affinities for the surface of fibers can be applied by exhaustion in dyeing machines, usually after the dyeing process has been completed.[49] In this process, the textile fabric is loaded into a machine containing the finishing chemical for a period of minutes to hours, depending on the time required for the chemical to react with the textile fabric.[50]

Padding is another process of applying repellent finishes to textile fabrics. This is the primary application process used in textile finishing. It involves passing the fabric through the chemical finish solution and then through two nip rollers to squeeze out excess solution, leaving the fabric with a certain amount of the chemical finish. The amount of the repellent finish imparted on the fabric is known as the "wet pickup." The wet pickup is affected by several factors such as the type of fiber, fabric construction, as well as the pressure of the squeeze nip rollers, temperature and concentration of the solution, and length of time during which the fabric was immersed in the chemical solution. In order to achieve a consistent application of the chemical finish on the fabric, the non-fabric related factors must remain constant throughout the application process.[51]

Repellent finishes can be sprayed directly onto fabric surfaces. Spraying delivers a set amount of the finish to the textile fabric which can be adjusted by controlling the flow rate. With spraying, it is possible to create uneven finishes from overlapping spray patterns. Spraying is commonly used for silicone-based repellent chemistries but can also be used with fluorinated DWR chemistries if a low level of the finish is required on the fabric and appropriate inhalation toxicity data is available to ensure safe use.[52]

Foams are used to apply finishes to textile fabrics to reduce the amount of water used in the finishing processes. With foams, water in the chemical finishing process is replaced with air. Foam generators produce foam with the required density which is applied to the fabric. A squeeze roller can then be used to ensure uniform application of the foams. Similar to spraying, foam application of fluorinated DWR chemistries is used when a low level of the finish is required.[53]

6. Performance attributes and requirements of treated textile fabrics

6.1 Types of fabric performance attributes

The performance of DWR finishes on textile products is a complex property to evaluate. Performance is not based on a single fabric attribute that a DWR finish delivers but instead, a combination of several attributes.

Taking into consideration the intended end use of the textile product, a fabric may require water repellency, water resistance, oil repellency and soil/stain release. In some cases, not all performance attributes are necessary on a fabric. On the other hand, some intended end uses of products may require multiple attributes on the same fabric. As such, the repellent finish applied on the fabric will have to provide all required attributes and at specified performance levels.

Repellent finishes are also required to permit the transfer of air and water vapor through fabrics (breathability) and be durable to repeated laundering and dry cleaning, as well as abrasion. Durability is measured using test methods after laundering, dry cleaning, abrasion, etc. to simulate actual uses of products (see Appendix A). For fabrics that may require only a single attribute for the intended use, there is the possibility that the level of performance of that attribute may be negatively affected by lack of other attributes in certain cases. For example, in the absence of oil repellency the performance of a fabric treated with a DWR finishes which only offers water repellency may be reduced when the surface of the fabric is stained by oily stains.

In addition to repellency and stain release, there are other important attributes that are considered in determining the performance of finishes. For example, repellent finishes applied on textile fabrics can impact fabric color, handle and tear strength. All these fabric attributes are essential for the end users of the textile products.

6.2 Repellents performance requirements and test methods

6.2.1 Performance requirements

The required performance level of DWR finishes depend on the intended use of the textile product in addition to fabric type, required fabric weight, and expected number of laundering cycles of product. There is not a single acceptable performance level for DWR finishes on textile products. Required performance levels are set by brands or retailers selling the finished textile products and vary considerably from one brand or retailer to the next and from one fabric or product to another, and often constitute intellectual property of the brand or retailer in question. The myriad fabric performance attributes and the performance requirements make it very challenging for the establishment of a generic performance criteria. For example, a retailer of a pair of slacks may require an initial water repellency rating of 80 and 70 after 20 home laundering cycles; and initial oil repellency rating of 4 and 3.5 after 20 home laundering cycles; and an initial stain release rating of 5 and 3.5 after the same number of home laundering cycles [as evaluated by AATCC test methods 22, 118 and 130, respectively (see section 6.2.2 below)]. Another retailer may only be concerned with water and would require just a water repellency test with different specifications or may use other test methods (either by the AATCC or another organizations) to evaluate the product's performance level.

There is a not a clear association between different fabric attributes. A DWR finish's ability to provide one attribute does not ultimately guarantee that it will also provide other attributes. There are some good repellents that are poor releases and vice versa. Even in the case of fluorinated DWR chemistries which can provide both water and oil repellency, there is still no clear association between water repellency and oil repellency attributes. Some fluorinated DWR chemistries are better on oil repellency while others are better water repellents.

6.2.2 Test Methods

Generally, test methods such as those developed by the American Association of Textile Chemists and Colorists (AATCC), International Organization for Standardization (ISO) and the American Society for Testing and Materials (ASTM) are employed in evaluating the performance levels of finishes applied on fabrics.

Similar to required performance levels, the test method employed in evaluating performance of fabrics or products also vary by brand or retailer. To add to the complexity of evaluating performance, more than one test method even from the same organization (e.g. AATCC) can used to evaluate the same fabric attribute.

The AATCC standardized test methods are the most widely used test methods in the textile industry. It is important to note that test results of all AATCC test methods and test methods from other organizations are numerically quantified. They do not define “passing” or “failing” for any test. The designation of what constitutes a “pass” or “fail” result for any test method is established individually by brands and retailers based on the results of the test methods and their required performance level of a textile fabric or product.

The following are some of the widely used test methods for fabrics treated with a repellent finish (see Appendix B for additional test methods).

Test method	Summary description
AATCC TM 22-water repellency: spray test	Water sprayed against the taut surface of a treated fabric under controlled conditions produces a wetted pattern. The size of the wetted pattern which depends on the relative repellency of the fabric is compared to a standard chart of fabric water repellency ratings of zero (0), 50, 70, 80, 90 and 100. A rating of zero (0) is assigned if the fabric’s surface is completely wetted by water, whereas a rating of 100 corresponds to no wetting of water on the surface of the fabric.
AATCC TM 35- water resistance: rain test	Water is sprayed on a treated fabric, backed by a weighed blotter paper, for 5 minutes under controlled conditions. The blotter paper is then reweighed to determine the amount of water which leaks through the fabric during the test. This test method measures the treated fabric’s resistance to rain penetration.
AATCC TM 42-water resistance: impact penetration test	A volume of water is spayed against the taut surface of a treated fabric backed by a weighed blotter paper. The blotter paper is then reweighed to determine the amount of water

	penetrating the fabric. This test method measures the treated fabric's resistance to penetration of water by impact.
AATCC TM 127-water resistance: hydrostatic pressure test	The surface of a treated fabric is exposed to hydrostatic pressure at a constant rate until three points of leakage appear on the other surface. This test method measures the fabric's resistance to penetration of water under hydrostatic pressure. The results of this test method may not be the same as those evaluating resistance to rain or spray water.
ISO 9865-water repellency: Bundesmann rain shower test	The treated fabric is mounted to a cup and then exposed to an artificial rain under defined conditions. The surface of the treated fabric is subjected to rubbing to simulate a user carrying a bag on the shoulder of a garment. This test measures the resistance of a fabric to the penetration of water. The water repellency of the fabric is assessed by comparison of the wet fabrics to a standard chart with rating of 1, 2, 3, 4 and 5. A rating of 1 is assigned if a fabric's surface is completely wet, whereas a rating of 5 corresponds to fast runoff of small water drops with no wetting on the fabric surface. Mass of the fabric is recorded before and after artificial rain exposure to determine the percent water absorbed in the fabric. Also, water is collected in the sample cup that has passed through the fabric and it volume (mL) and mass (g) recorded.
EN 14360–rain test (test method for ready-made garments)	This test method is a European standard that defines test conditions under which ready-made garments are exposed to heavy rain. It applies to garments such as jackets, trousers, coats, etc. This test method does not apply to the testing of garments for resistance to other weather conditions such as snow or strong winds.
AATCC TM 193-aqueous liquid repellency: water/alcohol solution resistance test	Drops of a selected series of water/alcohol solutions of different surface tensions are placed on a treated fabric surface and observed for wetting. This test method is used to evaluate the effectiveness of the finish in imparting a low surface energy on the surface of the treated fabric.
AATCC TM 118-oil repellency: hydrocarbon resistance test	Drops of eight selected liquid hydrocarbons of different surface tensions are placed on a treated fabric and observed for wetting. The oil repellency grade of the fabric is the highest numbered test liquid which does not wet the fabric surface with the highest achievable grade being 8. This test method is used to detect the presence of a finish capable of imparting a low energy surface on the treated fabric.
AATCC TM 130-soil release: oily stain release method	A stain applied on the treated fabric is forced into the fabric using a specified weight. The stained fabric is then laundered in a prescribed manner and the residual stain is compared to a graduated series of stains. This test method measures the ability of the fabric to release oily stains during home laundering.

Table 1: Test methods for fabrics treated with durable water repellent finishes

6.3 Actual industry practices in assessing performance of DWR finishes

Practical methods used in assessing the performance of DWR finishes on fabrics vary significantly by brand and/or retailer. This information is mostly considered intellectual property by most brands and retailers. With respect to the outdoor apparel industry, the typical approach for outerwear involves the use of AATCC test method 22, ISO 99865 (Bundesmann rain shower test) and AATCC test method 127.

For AATCC test method 22, a rating of 80 before and after 10 home laundering cycles is considered passing. This test method is required for rainwear customs duty. Bundesmann rain shower test is used to simulate actual use of textile products by end users. A rating of 4 after 10 minutes using the Bundesmann rain shower test is considered passing. AATCC test method 127 is only used on garments with taped seams. This method is used to assess the integrity of the taped seam bond, not the fabric, and it is a pass at 3 lbs after 10 minutes.

7. Health and environmental attributes of repellent chemistries

Repellency, stain release and other fabric attributes alone are not enough to determine the overall performance of a DWR finishes. The health and environmental attributes of repellent chemistries, including raw materials and byproducts are critical factors to consider in ensuring that DWR finishes are safe both for the end users of products and workers, and the environment. There are specific hazard endpoints that are used to evaluate the human health and environmental attributes of chemical substances (see Appendix C). They include acute and chronic mammalian toxicity, acute and chronic aquatic toxicity, and environmental toxicity and fate. These endpoints evaluate the intrinsic hazard of chemicals. Some hazard endpoints may be more critical than others depending on chemical uses and exposure potential. Evaluating the health and environmental attributes ensure that one potentially hazardous chemical is not replaced by another.

In assessing the potential health and environmental attributes of DWR chemistries, a comprehensive approach is required to address their overall impacts. Lack of an association to PFOA and PFOS should not be the only criteria used to assess potential impacts. Instead, the overall risk associated with the DWR chemistries, not just hazard alone, should be taken into account. As described above, chemistries that are not associated with PFOA and PFOS may be linked to other substances (either in the DWR finish or in the production process) of concern. By-products of short-chain fluorinated chemistries are persistent in the environment and are subject to use restrictions in certain countries. Although these by-products have been shown to be less toxic and bioaccumulative, their persistence is judged to be a characteristic of concern, particularly if they can be widely dispersed in the environment.

Non-fluorinated DWR chemistries are also not without human health and environmental concerns. Stearic acid-melamine chemistries may release formaldehyde during textile processing. And application processes used to apply silicone repellent finishes to textile products generate waste water that is toxic to fish. It should be noted that some DWR chemistries (e.g., chemistries containing dendrimers and nano-materials) are relatively new and may not be well studied. These chemistries may therefore lack enough data to perform assessments of their effects on human health and the environment. Lack of hazard data should not correspond to the assumption that these chemistries are safer or have favorable human health and environmental properties. Conducting a hazard assessment of DWR chemistries using the endpoints listed in Appendix C could help ensure that the impacts of chemistries, including impacts related to their raw materials and by-products are taken into consideration when selecting replacement chemistries for long-chain fluorinated DWRs.

8. Commercially available alternative DWR technologies and chemistries for textile applications

There were a limited number of chemical producers and/or suppliers who responded to the request for information on commercially available alternative DWR technologies and chemistries.

8.1 Short-chain fluorinated repellent chemistries

Information about commercially available alternative DWR finishes containing short-chain fluorinated chemistries received from the chemical producers contacted was predominantly repellent finishes product brochures. These repellent finishes claim to offer comparable or superior performance attributes associated with finishes containing long-chain fluorinated chemistries, including water and oil repellency and stain release. Nonetheless, not all the repellent finishes with short-chain chemistries are marketed as providing both repellency and stain release attributes. Depending on the manufacturer, some finishes containing short-chain chemistries are marketed for use on textile fabrics to provide either water and oil repellency or stain release.

Very limited information was provided regarding performance levels, methods used to evaluate the performance and other important attributes (such as durability to repeated laundering and dry cleaning, abrasion resistance and breathability) of these chemistries. There is a lack of an industry-wide performance standard against which the short chain fluorinated DWR chemistries can be evaluated. And since the performance requirements of repellent finishes vary from brand to brand, the provision of repellent finishes' performance levels for the different fabric attributes may have served little to no purpose in understanding actual performance levels for the different fabric types and their intended uses. The performance of repellent finishes varies from fabric to fabric and even for the same fabric with different intended uses.

Commercially available DWR finishes containing short-chain fluorinated chemistries vary considerably regarding the textile fabrics (or fibers) on which they can be applied. Few repellent finishes claim to have application on fabrics of all fiber types, whereas others claim to have applications on cotton, wool or synthetics and their blends. There were other repellent finishes that indicated the final product, rather than the fabric, on which they can be applied.

With respect to their potential health and environmental impacts, not all chemical producers provided actual hazard data on their repellent products. The few hazard data provided was not comprehensive across the list of hazard endpoints (Appendix C).

Some DWR finishes with short-chain fluorinated chemistries claim no association with both PFOA and PFOS. In other words, the chemistries do not break down in the environment into PFOA and PFOS. Other finishes claim to be PFOA- and/or PFOS-free, explaining that these chemicals may be present as impurities but below their levels of detection. It is unclear whether finishes that claim not to break down in the environment are also implying that PFOA and PFOS impurities are present but below detectable limits.

PFOA and PFOS are not the only possible degradation products of fluorinated substances. Other byproducts of these commercially available DWR finishes containing short-chain fluorinated chemistries may be substances of potential concern.

8.2 Non-fluorinated repellent chemistries

Commercially available non-fluorinated chemistries submitted by chemical producers included the acrylic- and urethane-based, as well as other conventional chemistries such as paraffin, silicone and stearic acid-melamine. These commercially available non-fluorinated chemistries only claim to provide water repellency. No non-fluorinated chemistry is marketed as a stain release finish. Similar to the short-chain chemistries, there was limited information provided on performance of these non-fluorinated chemistries.

8.3 Repellent chemistries identified through internet searches

Online journal search yielded no results on short-chain fluorinated chemistries. A search for short-chain fluorinated DWR chemistries in the *ScienceDirect*, *Wiley InterScience*, and other journal databases yielded several articles but contained no relevant information. Information about short-chain fluorinated chemistries was only available through chemical producers.

9. Recommendations

Moving from long chain to short-chain fluorinated DWR chemistries is a complex process. There are many product performance requirements to be met and other critical factors to take into account. The availability of alternative chemistries may be an indication that there is potential for substituting DWRs containing long-chain with short-chain fluorinated chemistries. Yet, the complexities of DWR chemistries and their applications require a thorough assessment of the available alternative short-chain chemistries to understand their potential applications. Additional research is needed in order to realize opportunities that exist and make an informed decision about when a move to short-chain DWR chemistries can occur. Sections 9.1 and 9.2 below provide some practical steps to address in follow up research projects in moving from long-chain to short-chain and non-fluorinated DWR chemistries.

One important aspect to consider in making chemical substitutions relates to their socio-economic impacts. Socio-economic impact assessment is designed to help in making decisions that promote long term sustainability of a proposed idea, including economic prosperity, improvements in the health of communities and social well-being. With respect to restricting the use of chemicals, socio-economic impact assessment helps in realizing the net benefits to human health and the environment, and the net costs to manufacturers, importers, downstream users, distributors, consumers and society as a whole. It also provides a comprehensive comparison between available risk management options on chemicals and proposed restrictions.

Under the European Union's chemical regulation, REACH, socio-economic impact assessment is considered to play a vital role in the process of restricting and authorizing the use of chemicals. The European Chemical Agency (ECHA) has been active in developing and promoting the application of socio-economic impact assessment in regulating chemicals. The agency is currently working to assess the cost associated with substituting substances with alternatives and has developed a technical guidance document on how to assess the socio-economic impact of substitutions.[54]

According to ECHA, any proposed restriction on the use of a chemical needs to demonstrate why the risk associated with the chemical should be managed at a community-wide level. The proposed restriction should be compared to other available options that can be used to manage the risk associated with the chemicals in question. It should then be assessed for the benefits and costs to human health, the environment and society as a whole.

9.1 Some practical steps for moving from long-chain to short-chain fluorinated DWR chemistries

(i) Identify product group using DWR finishes and their fabric types

Not all textile products are treated DWR finishes. As such, the initial step for moving from long-chain to short-chain fluorinated DWR chemistries may require brands to identify their products that are treated with DWR finishes. Since finishes are mostly applied to fabrics and that performance varies by fabric type, the fabric composition of products treated with DWR finishes should be noted.

(ii) *Define fabrics performance attributes and required performance levels, including durability requirements*

Depending on the intended use of products, a fabric may require one or more performance attributes. For the most part, brands are familiar with attributes desired on their products and test methods used to evaluate performance. Nonetheless, performance attributes for some brands may go beyond water and oil repellency and stain release. There is a myriad of other attributes that may be desired on products by some, but not all, brands. It is critical that brands recognize all desired fabric attributes for their products and their performance levels, including the required number of laundering cycles. Other important requirements such as weight of fabrics should be taken into account when defining requirements.

(iii) *Define desired environmental and health characteristics*

The human health and environmental attributes of DWR chemistries are as important as their performance levels. Recognizing the potential human health and environmental impacts of chemistries would ensure that substitute DWR chemistries are not equally or more hazardous than the finishes they replace. As such, brands should define the desired human health and environmental attributes of DWR chemistries supplied by chemical producers. There may be the need for prioritizing the comprehensive list hazard endpoints listed in Appendix C. In reality, chemical producers are not likely to have complete hazard data for their DWR finishes, raw materials and by-products. The criteria for evaluating human health and environmental impacts can perhaps be persistence, bioaccumulative and toxic (PBT). In addition, brands should require third party certification that short-chain fluorinated DWR chemistries are indeed not associated with PFOA and PFOS.

It should be noted that the long-chain fluorinated chemistries are well known and studied. On the other hand, short-chain fluorinated chemistries may lack enough data to enable assessments of their potential human health and environmental impacts. Brands should set strong requirements for chemical hazard data for short-chain fluorinated chemistries that are potential replacements for long-chain chemistries.

In addition to intrinsic hazards, the overall risk associated with the DWR chemistries should be taken into account. This would provide a better understanding of the true impacts of the DWR chemistries.

(iv) *Identify suppliers with alternative repellent chemistries that provide the defined attributes*

Short-chain fluorinated DWR chemistries marketed by chemical producers or suppliers do not all provide the desired attributes on fabrics. Some short-chain fluorinated chemistries may be better repellents than releases and other may be better releases than repellents. Additionally, some may be relatively more durable. To recognize the DWR chemistries that may be feasible alternatives, brands should contact chemical suppliers as inquire whether their short-chain fluorinated chemistries can meet their defined performance attributes and requirements.

(v) Collect environmental and health data on the repellent chemistries from chemical suppliers and assess the potential environmental and health impacts

For chemical suppliers who consent that their short-chain fluorinated DWR chemistries meet brands requirements, they should be made to provide data on their chemistries in order for brands to conduct appropriate hazard and risk assessments. Data that chemical suppliers provide should include data on raw materials and by-products. As mentioned above, it is likely that a comprehensive list of hazard endpoints would not be available. Persistence, bioaccumulative potential and toxicity can be used as the criteria to assess the impact of the alternative chemistries.

(vi) For chemistries meeting desired environmental and health standard, conduct pilot test of evaluate the performance using current practices and processes

Conducting a pilot test on the short-chain fluorinated DWR chemistries would help brands distinguish between feasible short-chain fluorinated chemistries from non-feasible ones for their product groups requiring DWR finishes. The test should be conducted using current practices and processes in facilities where DWR finishes are applied to fabrics, as this will ensure that the short-chain fluorinated DWR finishes can be successfully implemented. Other processes such as taping, printing, etc. should also be manufactured and tested to ensure that they are functional after application of DWR finishes. Brands may also inquire from their suppliers whether they can switch to alternative chemistries. The supplier of the alternative chemistry should provide support on-site in switching to alternative chemistries.

9.2 Some practical steps for moving from short-chain to non-fluorinated DWR chemistries

Some of the practical steps to address in follow up research projects to move from short-chain to non-fluorinated DWR chemistries are identical to the steps involved in moving from long-chain to short-chain fluorinated DWR chemistries. Nonetheless, these steps are only applicable to textile product groups that require water repellency in the case of non-fluorinated DWR chemistries. Since there appears to be no non-fluorinated chemistry that provides oil repellency and stain release attributes, fluorinated DWR chemistries may be the ideal chemistry to achieve these attributes on textile products. The move from short-chain to non-fluorinated DWR chemistries must commence with research and development efforts by chemical suppliers to identify chemistries with the potential to provide all the required fabric attributes associated with fluorinated DWR chemistries and at the preferred performance levels on fabrics.

10. Conclusion

Durable water repellents containing short-chain perfluoroalkyl functionality are currently promoted as viable alternatives to long-chain perfluoroalkyl functionality. Nonetheless, short-chain fluorinated DWR chemistries are known to be less effective in providing desired fabric performance attributes. In less critical applications, comparable performance levels to long-chain fluorinated DWR chemistries can be achieved by higher repellent application levels of short-chain fluorinated chemistries. With respect to critical applications, fabric performance levels are not yet achievable with short-chain fluorinated DWR chemistries. Although the desired performance levels for some application may be eventually achieved, there are other application for which short-chain chemistries may never be able to meet performance requirements.

Short-chain fluorinated chemistries are promoted as having favorable health and environmental properties. They are known to be less toxic and have low bioaccumulative potential. They are, nonetheless, associated with substances that may be of concern, particularly in cases where their use can result in widespread dispersion in aquatic environments. For some commercially available short-chain fluorinated DWR chemistries, there may be lack of enough data to allow for an assessment of their health and environmental impacts. Brands should set strong requirements for chemical hazard data for short-chain fluorinated DWR chemistries that are identified as potential alternatives to long-chain fluorinated chemistries. The overall risk associated with short-chain fluorinated chemistries should be taken into account, as this would provide a better understanding of the true impacts of these DWR chemistries.

Moving from long chain to short-chain fluorinated DWR chemistries is a complex process that requires an in-depth research in order to realize opportunities that exist and make an informed decision about when a move to short-chain fluorinated DWR chemistries can occur. Future research projects on this subject should consider, among other practical steps for moving from long-chain fluorinated chemistries, the overall risk and socio-economic impact associated with short-chain fluorinated chemistries. With respect to other practical steps, brands should initially identify their products that are treated with DWR finishes and be familiar with products performance attributes and requirements. Brands should then reach out to chemical suppliers with short-chain fluorinated DWR chemistries that can be used to achieve performance attributes and requirements. It is critical that the short-chain fluorinated DWR chemistries supplied by chemical producers, including their raw materials and by-products, are evaluated for their human health and environmental impacts. This will ensure that potential substitutes are not associated with substances having comparable health and environmental impacts as long-chain fluorinated chemistries. The short-chain fluorinated DWR chemistries that brands conclude to have favorable health and environmental impacts and chemical suppliers consent meet performance attributes and requirements should be pilot tested on products to guarantee that fabrics attributes and performance requirements can indeed be met.

The move from fluorinated to non-fluorinated DWR chemistries is much more challenging and one that also require an in-depth research to realize the practical application of non-fluorinated DWR finishes on textile products. Research and development efforts are also needed to make certain that non-fluorinated chemistries can provide the desired fabric attributes as well as meet their defined performance requirements. Presently, commercially available non-fluorinated chemistries do not provide oil repellent and stain release attributes on fabrics. These attributes, in addition to several others, are demanded for certain product groups by their end users.

11. Appendices

Appendix A: fabric types, end uses and performance requirements

(Developed by ZDHC, OIA, EOG Project Team)

Fabric	Fiber type	Weave	Types of product	Weight	End Use	Perform-ance require-ment as delivered	Perform -ance require-ment after wash	Durability	Wash methods*	Test Methods	EN & ISO Equivalents	Perform-ance benefit	Notes
WOVENS													
Lightweight denim.	cotton, cotton/ spandex	Twills	jeans, Truckers jackets, denim shirts	6 to 11 oz/ sqyd	Casual	80 4.0 5	70 3.5 3	20 wash and dry cycles	normal cycle. 40 C. Tumble dry med	AATCC 22 AATCC 118 AATCC 130	ISO 4920:2012 ISO 14419:2010 ISO 22958:2005	Water repellency, oil repellency, stain release	In some cases, not all 3 performance benefits are tested. Depends on product and Brand.
Heavy weight denim. Mostly Bottom weight	cotton, cotton/ spandex	Twills	jeans, Truckers jackets,	11 to 15 oz/sqyd	Casual	80 4.0 5	70 3.5 3	20 wash and dry cycles	normal cycle. 40 C. Tumble dry med	AATCC 22 AATCC 118 AATCC 130	ISO 4920:2012 ISO 14419:2010 ISO 22958:2005	Water repellency, oil repellency, stain release	In some cases, not all 3 performance benefits are tested. Depends on product and Brand.
Chambray casual tops	cotton, cotton/spandex	plain weave	shirts	4 to 6 oz/sqyd	Casual	90 5.0 5 5	80 4.0 3 3	20 wash and dry cycles	normal cycle. 40 C. Tumble dry med	AATCC 22 AATCC 118 AATCC 130 AATCC 193	ISO 4920:2012 ISO 14419:2010 ISO 23232:2009 ISO 22958:2005	Water repellency, oil repellency, stain release aqueous liq repellency	In some cases, not all performance benefits are tested. Depends on product and Brand. It should be easier to get higher performance with lighter weight fabrics

Lightweight non denim, mostly cotton blends	cotton, cotton/ spandex. cotton/poly blends, polyester	twills and plain weaves	Pants, shirts, shorts jackets	4 to 7 oz/sqyd	Casual	90 5.0 5 5	80 4.0 3 3	20 wash and dry cycles	normal cycle. 40 C. Tumble dry med	AATCC 22 AATCC 118 AATCC 130 AATCC 193	ISO 4920:2012 ISO 14419:2010 ISO 23232:2009 ISO 22958:2005	Water repellency, oil repellency, stain release aqueous liq repellency	In some cases, not all performance benefits are tested. Depends on product and Brand. It should be easier to get higher performance with lighter weight fabrics. Note, Dockers evaluates AATCC 193, 130 and 118 at 30 washes
Heavy weight non denim, mostly cotton blends	cotton, cotton/ spandex. cotton/poly blends, polyester	twills and plain weaves	Pants, jackets	7 to 11 oz/ sqyd	Casual	90 5.0 5 5	80 4.0 3 3	20 wash and dry cycles	normal cycle. 40 C. Tumble dry med	AATCC 22 AATCC 118 AATCC 130 AATCC 193	ISO 4920:2012 ISO 14419:2010 ISO 23232:2009 ISO 22958:2005	Water repellency, oil repellency, stain release aqueous liq repellency	In some cases, not all performance benefits are tested. Depends on product and Brand. It should be easier to get higher performance with lighter weight fabrics
Very lightweight cotton	cotton, cotton/ spandex.	plain weave	Jackets	150 g/ sqm	Performance Outerwear	90	80	20 wash and dry cycles		AATCC 22	ISO 4920:2012	Water resistance	Should this be "Rainwear" Could this fit in row 7
Lightweight synthetics	Nylon, polyester	plain weaves, dobbies	wind wear, rainwear	45-80 gm/m2	Performance Outerwear	90	80	20 wash and dry cycles		AATCC 22	ISO 4920:2012	water repellency	athletic use - may get washed frequently
Lightweight synthetics	Nylon, polyester	twills and plain weaves	Board shorts, rain jackets, wind wear	100-200 gm/m2	swimwear	90	80	20 wash and dry cycles		AATCC 22	ISO 4920:2012	quick dry (repellency)	less washing. Chlorine resistance
Heavy synthetics	Nylon, polyester	twills and plain weaves	Board shorts, rain jackets, wind wear	200-300 gm/m2	performance outerwear	90	80	20 wash and dry cycles		AATCC 22	ISO 4920:2012	quick dry (repellency)	less washing. Chlorine resistance. Should we call this rainwear?

Wool	2 layer waterproof breathable laminate polyester film	plain weave	Outerwear jackets	250 gm/m2	Performance outerwear	90	80	20 wash and dry cycles		AATCC 22	ISO 4920:2012	Water proof	Taped seams.
Wool and wool blends	Wool, wool/ polyester, wool/ cotton	twills and plain weaves	outerwear	250 gm/m2	Outerwear	90	80	hand wash, lay flat to dry		AATCC 23	ISO 4920:2012	Water repellency	Minimal washing
Tropical Wool	Wool	twills, herring-bones and plain weaves	Jackets, pants, skirts, suiting		Business casual and Business	90 5.0 5 5	80 4.0 3 3	10 wash and dry cycles. Should test dry cleaning	delicate wash. 30 C. No tumble dry	AATCC 22 AATCC 118 AATCC 130 AATCC 193	ISO 4920:2012 ISO 14419:2010 ISO 23232:2009 ISO 22958:2005	Water repellency, oil repellency, stain release aqueous liq repellency	In some cases, not all performance benefits are tested. Depends on product and Brand. It should be easier to get higher performance with lighter weight fabrics.
Suiting	Wool, poly/wool/ rayon	twills and plain weaves	Jackets, pants, skirts, suiting		Business	90 5.0 5 5	80 4.0 3 3	10 wash and dry cycles. Should test dry cleaning		AATCC 22 AATCC 118 AATCC 130 AATCC 193	ISO 4920:2012 ISO 14419:2010 ISO 23232:2009 ISO 22958:2005	Water repellency, oil repellency, stain release aqueous liq repellency	In some cases, not all performance benefits are tested. Depends on product and Brand. It should be easier to get higher performance with lighter weight fabrics.
Leather	leather	leather	jackets		Outerwear , casual				dry clean or no cleaning			water resistance	dry clean only
Feather and Down	polyester/ down	twill and plain weaves	jackets	50 gm/m2 (30 d)	Outerwear							Water resistance	dry clean only???? (Not required - laundering OK) Ultra Light

Pile fabrics - cotton or cotton blends	cotton and cotton/ polyester	corduroy and velvet	pants, shirts jackets		Casual			20 washes	normal cycle. 40 C. Tumble dry med			not sure	really hard to get performance. Is this a valid category for us?
GEAR AND SHOES													
Very Lightweight Fabrics	Nylon, polyester	plain weaves	tents	1 - 2.5 oz/sqyd	Performance	100-90 2100-1800 mm H20	90-80 2100-1800 mm H20	3 wash and dry cycles	wash cold/line dry = 1 cycle (dry each time)	AATCC 22 AATCC 127	ISO 4920:2012 ISO 811:1981	Water repellency Water resistance	Spot clean or cold water rinse, line dry (customer care). Must also pass flammability requirements.
Synthetics	Nylon, polyester	twills, and plain weaves	luggage, backpacks, shoulder bags	1.5 to 13 oz/sq yd	Performance	95 700 mm H20	80	5 wash + 1 dry	wash cold 5x then line dry 1x	AATCC 22 AATCC 127	ISO 4920:2012 ISO 811:1981	Water repellency Water resistance	Spot clean. Heavy abrasion during use is expected.
Leather	Leather	Leather	shoes									Water repellency	
Textile			shoes									Water repellency	
Very Lightweight Fabrics	Nylon, polyester	plain weaves	sleeping bags	0.75 - 2.5 oz/sqyd	Performance	95 300 mm H20	90 300 mm H20	10 wash and dry cycles		AATCC 22 AATCC 127	ISO 4920:2012 ISO 811:1981	Water repellency	
KNITS													
Pile fabrics - synthetic		pile knits	outerwear, vests		Casual to Performance	80	70	30 wash and dry cycles	normal cycle. 40 C. Tumble dry med	AATCC 22	ISO 4920:2012	water repellency, improved dry time	difficult to achieve performance
Knits casual mostly cotton	cotton and cotton/ polyester	knit	T shirts		Casual	5	3	20 washes	normal cycle. 40 C. Tumble dry low	AATCC 130			
Knits performance mostly synthetic	polyester, nylon	knit	shirts, yoga pants, jackets, gloves		Performance	100	80	20 wash and dry cycles	normal cycle. 40 C. Tumble dry low	AATCC 22	ISO 4920:2012	Improved dry time, occasionally water repellency	Frequent washing

Knits performance synthetic	Nylon, polyester	knit (hard face, pile back)	softshell-type outerwear		Performance	95	90	20 wash and dry cycles	normal cycle. 40 C. Tumble dry low	AATCC 22	ISO 4920:2012	water repellency, improved dry time	
Sweaters	cotton, wool, polyester, acrylic	knit	sweaters		Casual				normal cycle. 30 C. Tumble dry low				
Fleece	cotton and cotton/ polyester and polyester	knit, non woven	jackets, sweatpants, sweatshirts		Casual and Performance	80	70	30 wash and dry cycles	normal cycle. 40 C. Tumble dry med	AATCC 22	ISO 4920:2012	water repellency, improved dry time	

Appendix B: fabric performance attributes and their applicable test methods

The following lists and provides additional test methods used to evaluate the performance of DWRs on textile products and their descriptions.

Water repellency

AATCC test method 22-2001: spray test

The spray test method measures the resistance of fabrics to wetting by water. It is applicable to any textile fabric, but is especially suitable for measuring the water repellent efficacy of finishes applied to fabrics, particularly on plain woven fabrics. The test method is not intended for use in predicting the probable rain penetration resistance of fabrics, since it does not measure the penetration of water through the fabric. For this test method, water sprayed against the taut surface of a test specimen under controlled conditions produce a wetted pattern whose size depends on the relative repellency of the fabric. The wetted pattern on the fabric is compared with a standard chart of fabric water repellency ratings of 0, 50, 70, 80, 90 and 100. A rating of zero (0) is assigned to fabrics whose surfaces are completely wetted by water, whereas a rating of 100 corresponds to fabrics with no wetting of water on their surfaces. The results obtained with this test method depend primarily on the resistance to wetting or water repellency of fibers, yarns and finish of the fabric, and not upon the construction of the fabric.

Standard spray test ratings

Rating	Description
100	No sticking or wetting of upper surface
90	Slight random sticking or wetting of upper surface
80	Wetting of upper surface at spray points
70	Partial wetting of whole of upper surface
50	Complete wetting of whole of upper surface
0	Complete wetting of whole upper and lower surfaces

ISO 9865:1991 (E): textiles - determination of water repellency of fabrics by the Bundesmann rain-shower test

This method for evaluating the water repellency of textile fabrics involves the mounting of fabrics on cups and exposing the fabrics to artificial rain shower for a period of ten minutes under defined conditions. The testing atmosphere must have a relative humidity and temperature of 65 ±2 % and 20 ±2 °C, respectively. Rain shower equipment, a clamping device and a centrifuge are employed in the method. The diameter of the each raindrop produced by the rain shower equipment must be 4 mm and the water flow of the equipment can be adjusted to ensure that the flow of water per minute is 100 ±5 ml for a rain shower surface area of 100 cm^2. The vertical distance between the raindrop former and the center of the specimen surface must be 1500mm. Normal tap water with a temperature of 20 ±3°C can be used for the rain shower but it must be mechanically filtered to remove coarse contamination. The water repellency of the tested fabric is evaluated by visual comparison of the specimen at the end of the test with five reference photographs. Each photograph has a corresponding grade, one through five. Grade 1 corresponds to the "specimen wet through over complete surface," whereas grade 5 corresponds to "fast runoff of small drops." Mass of the fabric is recorded before and after artificial rain exposure to determine the percent water absorbed in the fabric. Also, water is collected in the sample cup that has passed through the fabric and it volume (mL) and mass (g) recorded.

Water repellency grades

Grade	Description
5	Fast runoff of small drops
4	Formation of large drops
3	Drops adhere to parts of the specimen
2	Specimen partly wetted
1	Specimen wet through over complete surface

ISO 4920:2012 – determination of resistance to surface wetting (spray test)

This test method specifies a spray method for determining the resistance of any fabric, which might or might not have been given a water resistant/repellent finish, to surface wetting by water. It is not intended for use in predicting the rain-penetration resistance of fabrics, since it does not measure penetration of water through the fabric.

ISO 23232:2009 – aqueous liquid repellency (water/alcohol solution resistance test)

This test method is used to determine fabrics resistance to aqueous stains. The higher the aqueous liquid repellency grade, the better the resistance to staining by water/alcohol-based substances, especially water/alcohol-based liquids. It is not intended to give an absolute measure of the resistance of fabrics to staining by water/alcohol-based substances. Other factors, such as the composition and viscosity of the water/alcohol-based substances, fabric construction, fiber type, dyes and other finishing agents also influence stain resistance. In addition, it is not intended to estimate the resistance to penetration of fabrics by water/alcohol-based chemicals. The test method can also be used for determining if washing and/or dry-cleaning treatments have any adverse effects on the aqueous liquid repellency characteristics of fabrics.

AATCC test method 193-2007: water/alcohol solution resistance test

This test method can be used to determine the efficacy of a protective finish that is capable of imparting a low energy surface on all types of fabrics, by evaluating fabrics' resistance to wetting by a selected series of water/alcohol solutions of different surface tensions. In performing this test, drops of standard test liquids consisting of a selected series of water/alcohol solutions with varying surface tensions are placed on the fabric surface and observed for wetting, wicking and contact angle.

Water resistance

AATCC test method 35-2000: rain test

The rain test method measures fabrics resistance to the penetration of water by impact. Consequently, it can be used to predict the probable rain penetration resistance of fabrics. It is especially suitable for measuring the penetration resistance of garment fabrics. In performing this test method, a test specimen backed by a weighed blotting paper is sprayed with water for 5 minutes under controlled conditions. The blotting paper is then reweighed to determine the amount of water which has leaked through the specimen and onto the blotter during the test. Water penetration as indicated by the increase in mass of the blotting paper during the 5 minutes test period is calculated, and the average of 3 test specimens is documented. Individual and average values of over 5 grams are reported as 5+ or >5. In contrast to the AATCC test method 22-2001, this test method provides no rating for the rain penetration resistance of fabrics. It appears that it is at the discretion of users of this test method to define an amount of leaked water that will correspond to a high, medium or low rain penetration resistance of fabrics. The results obtained with this test method depend on the water repellency of the fibers and yarns, and on the construction of the fabric.

AATCC test method 42-2007: impact penetration test

This test method measures the resistance of fabrics, which may or may not have been given a water-repellent finish, to the penetration of water by impact. It can, thus be used to predict the probable resistance of fabrics to rain penetration. In conducting this test, a volume of water is sprayed against a taut surface of fabrics backed by a weighed blotter paper. The blotter paper is then reweighed to determine the amount of water penetrating the fabric. The results obtained with this test method depend on the water repellency of the fibers and yarns and on the construction of the fabric.

AATCC test method 127-2008: hydrostatic pressure test

This test method measures the resistance of fabrics, which may or may not have been given a water resistant/repellent finish, to the penetration of water under hydrostatic pressure. In conducting this test, the surfaces of fabrics are exposed to hydrostatic pressure at a constant rate until three points of leakage appear on the other surface. The water resistance of fabrics depends on the repellency of the fibers and yarns, as well as the fabric construction. The results obtained by this method may not be the same as the results obtained by AATCC methods for resistance to rain or water spray.

EN 14360:2004 – protective clothing against rain (test method for ready-made garments)

This test method is a European standard that defines test conditions under which ready-made garments are exposed to heavy rain. It applies to garments such as jackets, trousers, coats etc. This test method does not apply to the testing of garments for resistance to other weather conditions such as snow or strong winds.

ISO 22958:2005 – water resistance rain test (exposure to a horizontal water spray)

This test method also measures the resistance of fabrics, which may or may not have been given a water-resistant/repellent finish, to the penetration of water by impact. It can be used to predict the probable rain penetration resistance of fabrics. It is especially suitable for measuring apparel fabrics. Tests may be made at different intensities of water impact to give a complete picture of the penetration resistance of a single fabric or combination of fabrics. It is particularly suitable when measuring highly water resistant fabrics with low amounts of water penetration.

Oil repellency

AATCC test method 118-1997: hydrocarbon resistance test

The hydrocarbon resistance test detects the presence of a fluorochemical finish or other compounds capable of imparting a low energy surface on all types of fabrics. This test method evaluates fabrics resistance to wetting to a selected series of liquid hydrocarbons of varying surface tensions. The method is performed by placing drops of the standard test liquids on the fabric surface and observing for wetting, wicking and contact angle. Wetting of the fabric is demonstrated by a darkening of the fabric at the liquid-fabric interface, wicking and/or loss of contact angle of the drop. Different types of wetting may be encountered depending on the applied finish, fiber, construction, etc. and the determination of the end point of wetting can be difficult on certain fabrics. On black or dark fabrics, wetting can be identified by loss of "sparkle" within the drop. Each standard test liquid has a corresponding oil repellency grade. The oil repellency grade of the fabric is the highest numbered test liquid which does not wet the fabric surface, with the highest achievable grade being 8. A grade of zero (0) is assigned to a fabric which fails the Kaydol test liquid.

Standard test liquids

AATCC oil repellency grade number	Composition
0	None (fails Kaydol)
1	Kaydol
2	65:35 Kaydol:n-hexadecane by volume
3	n-hexadecane
4	n-tetradecane
5	n-dodecane
6	n-decane
7	n-octane
8	n-heptane

ISO 14419:2010 – oil repellency (hydrocarbon resistance test)

This test method is used to evaluate fabrics resistance to absorption of a selected series of liquid hydrocarbons of different surface tensions. Generally, the higher the oil repellency grade, the better resistance to staining by oily substance, especially liquid oil substances. This is particularly true when comparing various finishes for a given fabric. The test method is not intended to give an absolute measure of the resistance of fabrics to staining by all oily substances. Other factors, such as composition and viscosity of the oily substances, substrate construction, fiber type, dyes and other finishing agents, also influence stain resistance. It is also not intended to estimate the resistance to penetration of fabrics by oil-based chemicals. This test method can also be used in determining if washing and/or dry cleaning treatments have any adverse effect on the oil repellency characteristics of fabrics.

Soil release

AATCC test method 130-2000: oily stain release method

The soil release test method is designed to measure the ability of fabrics to release oily stains during home laundering. For this test method, a stain is applied to a test specimen and an amount of the staining substance is forced into the fabric. The stained fabric is then laundered in a prescribed manner and the residual stain is rated on a scale from 5 to 1 by comparing it to a standard graduated series of stains. A grade of 5 represents the best stain removal and grade 1 the poorest stain removal.

Stain release grades

Grade	Description
5	Stain equivalent to Standard Stain 5
4	Stain equivalent to Standard Stain 4
3	Stain equivalent to Standard Stain 3
2	Stain equivalent to Standard Stain 2
1	Stain equivalent to Standard Stain 1

Durability

The durability of a DWR finish is measured using applicable test methods after repeated laundering, dry cleaning and abrasion.

Repeated laundering: The performance of a DWR finishes on fabrics and many other fabric attributes are influenced by the manner in which fabrics are laundered. Generally, repeated laundering reduces the performance DWR finishes on fabrics. In other words, laundering reduces the ability of DWR finishes to repel water, resist water, repel oil and release stains on fabrics. Although it is designed to evaluate the smoothness of fabrics after repeated home laundering, the AATCC test method 124-2011 is also the primary test method employed in evaluating the durability of DWR finishes on fabrics.

AATCC test method 124-2011: smoothness appearance of fabrics after repeated home laundering

This test method is designed to evaluate the smoothness appearance of flat fabric specimens after repeated home laundering, but it is also used to determine the durability of finishes applied on fabrics in the textile industry. Fabrics of any construction, such as woven, knit and non-woven may be evaluated according to this method. Fabric specimens are subjected to standard home laundering practices. A choice is provided of hand or machine washing, alternative machine wash cycles and temperatures, and alternative drying procedures.

Laundering equipment

In using test methods which includes procedures for laundering (e.g. AATCC test method 124-2011), the AATCC has developed a set of guidelines for all test methods involving home laundering. These guidelines, AATCC monograph M6 – Standardization of Home Laundry Test Conditions, specifies the temperature, washing machine parameters for both top-loading and front-loading washing machines, as well as drying procedures for laundering.[55] The guidelines establish consistent conditions and are intended to reflect actual consumer practices. Tables I to VI below are the AATCC set of guidelines.

Table I: Temperature used in top-loading washing machines

Designation	Wash temperature	Rinse temperature
I	Very cold: 16 ± 3°C (60 ± 5°F)	<18°C (65°F)
II	Cold: 27 ± 3°C (80 ± 5°F)	<29°C (85°F)
III	Warm: 41 ± 3°C (105 ± 5°F)	<29°C (85°F)
IV	Hot: 49 ± 3°C (120 ± 5°F)	<29°C (85°F)
V	Very hot: 60 ± 3°C (140 ± 5°F)	<29°C (85°F)

Table IIA: Top-loading washing machine parameters without load 2011

Cycle	Normal[i]	Permanent press[ii]	Delicate[iii]
Water level medium[iv]	19 ± 1 gal	19 ± 1 gal	19 ± 1 gal
Agitation speed	86 ± 2 spm[v]	86 ± 2 spm	27 ± 2 spm
Washing time	16 min	12 min	8.5 min
Spin speed	660 ± 15 rpm[vi]	500 ± 15 rpm	500 ± 15 rpm
Final spin time	5 min	5 min	5 min

Table IIB: Top-loading washing machine parameters without load 2009-2010

Cycle	Normal	Permanent press	Delicate
Water level medium	18 ± 1 gal	18 ± 1 gal	18 ± 1 gal
Agitation speed	179/119 ± 2 spm	179/119 ± 2 spm	119 ± 2 spm

[i] Normal cycle is generally the cycle with the highest agitation and spin speed and it is also frequently designated as “heavy duty” or “ultra clean.”
[ii] Permanent press cycle is generally the cycle with the shortest final spin time to minimize wrinkle formation and it is also frequently designated as “easy care.”
[iii] Delicate cycle is generally the cycle with the shortest washing time and it is also frequently designated as “gentle.”
[iv] Water level for washing medium-sized loads
[v] spm = strokes per minute
[vi] rpm = revolutions per minute

Washing time	12 min total (6 min at step down agitation)	9 min total (3 min at step down agitation)	6 min
Spin speed	645 ± 15 rpm	430 ± 15 rpm	430 ± 15 rpm
Final spin time	6 min	4 min	3 min

Table IIC: Top-loading washing machine parameters without load 2000-2008

Cycle	Normal	Permanent press	Delicate
Water level medium	18 ± 1 gal	18 ± 1 gal	18 ± 1 gal
Agitation speed	179 ± 2 spm	179 ± 2 spm	119 ± 2 spm
Washing time	12 min	10 min	8 min
Spin speed	645 ± 15 rpm	430 ± 15 rpm	430 ± 15 rpm
Final spin time	6 min	4 min	6 min

Table IID: Top-loading washing machine parameters without load 1992-1999

Cycle	Normal	Permanent press	Delicate
Water level medium	18 ± 1 gal	18 ± 1 gal	18 ± 1 gal
Agitation speed	179 ± 2 spm	179 ± 2 spm	119 ± 2 spm
Washing time	12 min	10 min	8 min
Spin speed	645 ± 15 rpm	430 ± 15 rpm	430 ± 15 rpm
Final spin time	6 min	4 min	6 min

Table III: Temperature used in front-loading washing machines

Designation	Wash temperature	Rinse temperature
I	Tap cold	Tap cold
II	Cold: 20 ± 3°C (68 ± 5°F)	20 ± 3°C (68 ± 5°F)
III	Warm: 32 ± 3°C (90 ± 5°F)	20 ± 3°C (68 ± 5°F)
IV	Hot: 49 ± 3°C (120 ± 5°F)	20 ± 3°C (68 ± 5°F)
V	Very hot: 71 ± 3°C (160 ± 5°F)	20 ± 3°C (68 ± 5°F)

Table IV: Front-loading washing machine parameters

Cycle	Normal	Permanent press	Delicate
Water level (8lb load)[vii]	5.75 ± 1 gal	5.75 ± 1 gal	5.75 ± 1 gal
Soil level[viii]	Normal	Normal	Normal
Agitation speed	40 rpm	30 rpm	30 rpm
Washing time	18 min	16 min	14 min
Number of rinses[ix]	2	2	2
Final spin speed	1100 ± 100 rpm	800 ±100 rpm	400 ± 100 rpm
Final spin time	9.5 min	6 min	3 min

[vii] Water volume in high efficiency machines is determined by an automatic wash load detection system.
[viii] Wash time is dependent on soil level selected. Selecting "heavy" soil level will increase the wash time, whereas "light" or "extra light" will decrease the wash time.
[ix] Most front loading machines have an option to include an extra rinse in addition to the standard machine setting.

Table V: Drying Procedures

Designation	Drying Techniques
A	Tumble
B	Line
C	Drip
D	Screen
E	Flat bed press

Table VI: Tumble drying conditions

Drying Designation	Cycle	Maximum exhaust stack temperature with loaded dryer[x]
A	Normal or permanent press	65 ± 6°C (150 ± 10°F) [67 ± 6°C (154 ± 10°F) after 1983]
B	Delicate, synthetic, low	<60°C (140°F) [<62°C (144°F) after 1983]
Cool down time	Normal and delicate	5 min
	Permanent press	10 min
	All	10 min after 1983

According to AATCC, washing machines and dryers from Whirlpool, Kenmore, and Maytag are available that meet the parameters prescribed in its guidelines of laundering test condition. Below are the washing machines and dryer models from the above mentioned brands that meet the test conditions:[56]

Washing machines and dryers meeting standard laundering conditions

Washing Machines	Dryers
U.S. models, 60Hz	
Whirlpool: WTW4800X	Whirlpool: WED5500X; WED5550X; WED5600X
Kenmore: 26-21202; 26-20022; 26-21102	Kenmore: 66002; 68002
Maytag: MVWC200X	Maytag: MEDX550X; MEDX600X; MEDX700X
International models, 220V/60Hz	
Whirlpool: 4PWTW5905	Whirlpool: 3LWED5500X; 4GWED5500X
International models, 220V/50Hz	
Whirlpool: 3XWTW5705; 3LWTW4740YQ; 3DWTW4740YQ; 3LWTW4800YQ; 3SWTW4800YQ; 3LWTW4840YW; 3DWTW4840YW	Whirlpool: 3XWED5705; 3XLER5437

Laundry detergents

The purchase of commercial laundry detergents for use in testing labs is a fairly common practice. This is a result of several factors including the convenience of buying locally, price and the false assumption that the compositions of the same detergent

[x] The temperature of dryer exhaust should be measured at the end of the drying cycle before any cool down.

brand are similar and remain unchanged year after year. Commercial detergent products are constantly changing and this trend is anticipated to continue due to availability of and cost of materials, product costs, energy conservation, and environmental concerns. Commercially purchased detergents that are used in testing labs may have an effect on test results as they add inconsistencies to test methods. As such, the AATTCC has developed the AATCC standard reference detergent and laundry detergents to allow for reliable and consistency in duplication of testing. The traditionally used detergent, AATCC Standard Reference Detergent 124, was replaced with a newly formulated 1993 AATCC Standard Reference Detergent powder to be in agreement with typical commercial detergent products on the market and also tackle the environmental concerns with the use of phosphates in detergents.[57]

Laboratory comparisons indicated that the 1993 AATCC Standard Reference Detergent powder was not significantly different from the traditional standard reference detergent, except for oily stain removal. The 1993 AATCC Standard Reference Detergent powder was not as effective in removing oily stains. According to AATCC, comparisons between the 1993 AATCC Standard Reference Detergent powder and currently marketed products would likely show differences in washing performance, as will comparisons among marketed products. In some cases, the difference in washing performance of currently marketed products may be greater.[58]

Based on the increased market share of liquid laundry detergents, the AATCC developed the 2003 AATCC Standard Reference Liquid Laundry Detergent to be able to test products that are relevant to the current laundry market. Contrary to powder detergents which perform optimally at higher pHs (approximately 10), liquid laundry detergents perform optimally at pH at about 8.5. Since this pH is closer to neutrality, liquid laundry detergents tend to be less harsh on fabrics and dyes. With respect to overall performance and performance on individual stains, the 2003 AATCC Standard Reference Liquid Laundry Detergent’s stain removal profile has been shown to be comparable to five nationally marketed liquid laundry detergents.[59] AATCC has approved the addition of the 2003 AATCC Standard Reference Liquid Laundry Detergent as an alternative to 1993 AATCC Standard Reference Detergent powder in several of its test methods. The AATCC test method 124-2011 (smoothness appearance of fabrics after repeated home laundering) includes the liquid detergent option.[60] It should be noted that the standard detergent described above is applicable to the U.S. Different standard detergents are used in Europe and Asia.

There is no prescribed number of laundering cycles that can be used to evaluate the durability of DWR finishes. Individual brands set their own number of laundering cycles to evaluate the durability of DWR finishes. The number of laundering cycles depends on products intended uses and necessary performance levels. It can be as a small as five laundering cycles from products that require minimal washing. For high performance applications, the number of laundering cycles may be significantly greater. High performance products include products finishes that are intended to withstand high abrasion, strong rain and aggressive stains.

ISO method 6330:2012 – domestic washing and drying procedures for textile testing

This test method describes home washing and drying procedures for textile testing.

Japanese home laundering method JIS LO217, No. 213

This test method describes Japanese home washing and drying procedures for textile testing.

Abrasion resistance

Abrasion resistance: No test method was found in the 2002 *AATCC Technical Manual* for evaluating DWR resistance to abrasion. The AATCC test method for abrasion resistance is irrelevant to abrasion resistance of DWR finishes. This is because the test method, AATCC test method 93-2011, is intended to specifically evaluate the resistance of the fabric itself to abrasion, not the DWR finishes applied on fabrics.

Breathability

Similar to abrasion resistance, no AATCC test method for air permeability (breathability) of fabrics was found in the 2002 Technical Manual. Nonetheless, the American Society for Testing and Materials (ASTM) D737 test method is available to measure the air breathability of fabrics and it applies to most fabrics.

Other performance attributes

Test methods from both AATCC and ASTM for evaluating DWR effects on fabric color, weight and feel are not available. Companies may have devised specific procedures to evaluate these properties on DWR-finished fabrics.

Appendix C: human health and environmental hazard criteria

The hazard endpoints listed below are the criteria to be used to assess the human health and environmental impacts of the raw materials, products and byproducts of the alternative durable water repellent (DWR) chemicals. The hazard endpoints were adopted from the U.S. EPA *Design for the Environment (DfE)* program and the Clean Production Action *Green Screen* chemicals alternatives assessment tools.

Human Health Effects (aligned with P07 chemical hazard assessment criteria)

Carcinogenicity	
IARC classification	
GHS category	
Mutagenicity/genotoxicity	
GHS category	
Reproductive and developmental toxicity	
Oral (mg/kg/day)	
Dermal (mg/kg/day)	
Inhalation – gas/vapor (mg/L/day)	
Inhalation – dust/mist/fumes (mg/L/day)	
Endocrine Activity	
Evidence of endocrine activity	
Acute mammalian toxicity	
Oral LD50 (mg/kg)	
Dermal LD50 (mg/kg)	
Inhalation LC50 – gas/vapor (mg/L)	
Inhalation LC50 – dust/mist/fumes (mg/L)	
Repeated dose systemic toxicity/organ effects	
Oral (mg/kg-bw/day)	
Dermal (mg/kg-bw/day)	
Inhalation – gas/vapor (mg/L/6hr/day)	
Inhalation – dust/mist/fumes (mg/L/6hr/day)	
Skin sensitization	
GHS category	
Neurotoxicity	
GHS category	

Respiratory sensitization	
GHS category	
Irritation/corrosivity	
Eye irritation/corrosivity	
Skin irritation/corrosivity	

Environmental Toxicity and Fate

Acute aquatic toxicity	
LC50 or EC50 – fish, daphnia, algae (mg/L)	
Chronic aquatic toxicity	
LOEC – fish, daphnia, algae (mg/L)	
Environmental persistence	
Persistence in water, soil or sediment (half-life in days)	
Persistence in air (half-life in days)	
Bioaccumulation	
Bioaccumulation factor (BAF)	
Bioconcentration factor (BCF)	
Log BCF/BAF	

Sources:

U.S. EPA, *Design for the Environment (DfE) Program Alternatives Assessment Criteria for Hazard Evaluation Version 2.0*, August 2011. Available at http://www.epa.gov/dfe/alternatives_assessment_criteria_for_hazard_eval.pdf

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