While C8 fluorocarbons are being actively phased out of durable water repellent (DWR) finishes, the race for alternatives continues unabated. No single, all-encompassing, high performance solution leads, as yet.

The new state of DWRs



One year ago this month, when Greenpeace's 'Chemistry for any weather' report revealed the presence of PFCs in garments treated with a water repellent finish, even those declared to be PFC-free, it rekindled a long-standing debate in the chemicals and outdoor apparel industries. Perflourinated chemicals, or PFCs, used to make water-repellent garments, are problematic because of a by-product of their synthesis, perfluorooctanic acid (PFOA), widely recognised as dangerous for its persistent, bio-accumulative and toxic properties. PFOS, another by-product of PFC processing, has already been eliminated and can no longer be found – in any measurable quantity – in consumer goods.

The issue is deemed sufficiently preoccupying (carcinogenic to be precise) that the US Environmental Protection Agency (EPA) set up a PFOA Stewardship Programme in 2006. The eight members, major chemicals companies, pledged to reduce the presence of PFOA by



Water repellent finish Purtex WR, developed by Freudenberg, is based on polyurethane which it says "forms a three dimensional network around each individual fibre."

Freudenberg Purtex

2015. Though information on progress is limited, if this voluntary phase-out programme is successful, not only will water and oil-repellent finishes be PFOA-free in 2015, but also other PFC-based materials, such as PTFE (but that's another story).

The shift from C8 to C6

The simple way to reduce the amount of PFOA produced in water repellent finishing manufacturing is to switch from what is called long-chain C8 chemistry to C6 or C4

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On a mission to be Europe's most sustainable outdoor brand by 2015, Vaude has adopted a clear PFC-free stance. "If consumers were aware of the impact of PFCs, they would not want to buy a PFC-treated product," says Hilke Patzwall, the company's Sustainability & CSR manager.

Vaude

formulations. Known as short-chain, these contain either six or four fluorinated carbon atoms instead of eight, they offer similar properties to conventional C8, but are considered less stable, meaning they will break down faster in the environment, and will therefore be less durable when applied on textiles. Many sportswear brands are in the process of shifting to short chain fluorocarbons, but some high performance companies are still reluctant to "downgrade" their water-repellent features. Patagonia, for instance, says the majority of its current product range, carrying the Deluge DWR label, is still based on C8 formulations.

Most chemicals manufacturers have developed fabric finishes based on short chain chemistry. The shift to C6 is a logical move, though some suspect that companies will be tempted to apply 50% more product to achieve desired performance levels. Huntsman Textile Effects and DuPont have launched a short-chain version of Phobol, sold under the Teflon trademark. At Archroma (formerly Clariant), Nuva is now a PFOA-free C6 treatment. First introduced in 2006, it was the subject of heavy investment in 2012. Rudolf Group, in Germany, has joined forces with Swiss-based HeiQ to offer several DWR solutions with or without fluorocarbons, which will be marketed under HeiQ's brand Barrier. Rudolf markets its own finishes under the Bionic Finish Eco or short-chain C6 Ruco-Dry label.

Schoeller Technology's Nanosphere treatment has also shifted to C6 chemistry: "We view it as a good alternative in terms of performance," says marketing manager Lien Huynh, adding that it lasts 40 washes minimum and has been OK'd by bluesign.

Under the banner of a new catchphrase, Target C0 (for C-zero), Sympatex, the maker of a polyester membrane, has partnered with Rudolf to offer an entirely PFC-free waterproof-breathable solution encompassing both the membrane and topical fabric finish. Sympatex says it stopped using C8 chemistry in 2008, and promotes Rudolf Chemie's Bionic Finish Eco. "It is the product that offers the best results so far in terms of performance and durability," says Dr. Martin Meyershofer, the German company's head of research & development. The mid-term task is to add soil repellence to this "C0 chemistry".

At a conference for the campaign launch, Dr Meyershofer said that while C8 chemistry is known to be bio-accumulative and very persistent in the environment, the short chain versions, C6 and C4, are also considered persistent, though not bio-accumulative. "They are expected to be less harmful, but the data is limited," says Dr Meyershofer, adding that "C0 is a young technology compared to C8; we need further scientific research, and it is not yet proven that C0 is not harmful."

Fluorine-free dendrimers

The PFC-free "C0" Sympatex refers to is Rudolf Group's Bionic Finish Eco. Its water-repellent properties are based on dendrimers, 3D tree-like structures that keep water from penetrating a fabric (the term derives from 'dendron', the Greek word for tree). Rudolf describes dendrimers as "a hydrocarbon matrix and hyper-branched star-shaped polymer with terminal CH_3 groups, which, once cured, co-

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Sympatex says it stopped using C8 chemistry in 2008, and promotes Rudolf Chemie's PFC-free Bionic Finish Eco, based on polyurethane and dendrimers.

Sympatex

crystallise" in orderly patterns. It is a two-layer approach as the dendrimers are placed over a "comb-shaped" polyurethane polymer. No heating is required after washing, and the garments can be air-dried. Despite its fancy molecular structure (produced in a step-by-step process which in all likelihood must be delicate to master), the treatment only repels water, not oil.

Freudenberg is also presenting a PFC-free polyurethane fabric finish in its Purtex range. It "forms a three-dimensional network around each individual fibre," said Dr Birgit Severich, Purtex business manager at Freudenberg, at a press conference held at ispo 2013. The company has developed two versions, one that repels water (Purtex WR), with a wash durability said to be 30 cycles at 60°C, and one that is hydrophilic (Purtex WA, to improve the wearer comfort of synthetic fibres). Like all PFC-free finishes, Purtex WR does not protect the fabric from oily stains. "But the fine network does stop soil from seeping into the fabric, offering a type of soil release," said Dr Severich. Freudenberg is especially proud of the level of abrasion resistance achieved by the finish: "It is better by a factor of 4 to 8," said Ulrike Meissner, Purtex sales manager for Europe. She also points out that no free isocyanides – another class of dangerous chemicals – are released, throughout the process, saying, "this is an issue we have addressed from the earliest stage of production."

Hydrocarbon alternatives

One group of alternative DWR options trades fluorine for hydrogen atoms. The hydrocarbon bond is of a similar strength to that of C6 chemistry, offering comparable wash durability, ideally followed by a blast of heat to realign and reactivate the protective barrier.

Swedish University start-up Organoclick has developed a plant-based water-repellent finish. The textile version (other applications include wood and paper), Organotex, was launched at ispo in 2013 and is currently being tested by Scandinavian brands. Biodegradability is the innovative product's key environmental claim. "Our point is to offer the most eco-friendly treatment. The fact that our finish is biodegradable helps prove that Organotex does not bio-accumulate," says Robin Grankvist, business area manager for performance textiles.

Organoclick's process is based on what the company calls "organo-catalytic click



Abrasion resistant and biodegradable, Eco-repel is Schoeller Technologie's answer to those looking for ecological PFC-free water and soil repellent fabric treatments.

Schoeller Technologies

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PFOA limits today
(for a 200 g/m² of fabric)

- 100 µ/kg by Oekotex 100 class 1 standard
- 40 µ/kg by bluesign standard
- PFOS is limited to 1 µ/m2

chemistry", a method that bonds alkyl-functionalised polymers to a substrate. "Alkyls are long-chain carbon and hydrogen molecules, which are hydrophobic. In our process, a strong covalent bond attaches the finish to the fibre in a 3D pattern, which lowers surface tension. It repels water but is not oleophobic," says Mr Grankvist. The treatment is applied using conventional techniques, padding and curing, while energy and water consumption is also similar to usual processing.

Organotex is said to withstand 20 washes, a bit lower than the C6 treatments currently available. "20 washes is usually sufficient for outdoor apparel," says Mr Grankvist, adding that "consumers need to start washing less frequently and at lower temperatures, for the sake of the environment."

Ecorepel is Swiss-based Schoeller Technologies' (the chemicals branch of the textile manufacturer) answer to those looking for a PFC-free solution. In development since 2007, the biodegradable finish was officially launched in January 2012. The paraffin-based chemistry (paraffin is a hydrocarbon) is made of what the firm calls "long paraffin chains that wrap themselves spiral-like around individual fibres, filaments or yarns in a very fine film." This is said to reduce surface tension so that water droplets run off the garment. The breathability of the fabric is not affected, nor is its hand or feel. Ecorepel does not however possess stain release properties. "No fabric finish really releases a stain when it has been rubbed into the fabric, as it often is in real life," says marketing manager Lien Huynh, noting that when the stain is simply "rinsed off, without rubbing, both water and soil will roll off." Among its other properties, Ecorepel is said to offer good abrasion resistance, and to withstand 30 wash cycles at 40°C, but it cannot be dry-cleaned. Finally, compared to the company's other DWR treatment, Nanosphere, Ecorepel is lower priced.

US-based Nano-tex has also opted for a hydrocarbon formulation for its PFC-free water repellent finish Aquapel. Silicone is another option, developed by Elemental Technology, a new company based in Indonesia and with production facilities, in Italy. But here again, the substance is fine for water repellence and not much help for oily stains.

One year away from the 2015 deadline, no easy solution has yet to respond to all needs. Fluorocarbons, in their less preoccupying version, are the only finishes that protect a garment from water, oil and soil. None of the many alternatives possess these properties that are specific to PFCs. The question of whether outdoor garments need oil repellency is often raised. But grass, sunscreen, and eating are all a part of outdoor life. What all the alternative chemistries do however share is reduced durability, essentially removing the D from DWRs.

