GreenShield®

Fluorocarbons and Fabric Finishing

It has been found necessary to use fluorocarbon chemicals to produce the water repellency, oil repellency, stain resistance and removal performance that is now expected of fabrics in many situations, including sporting apparel, upholstery, wall covering, floor covering, and etc. Other materials can be made to perform some of these functions but suffer when subjected to oil and are considerably less durable.

Originally, small molecules like perfluorooctanoic sufonate (PFOS) and perfluorooctane sulfonamide (PFOSA) were used in products like 3M's Scotchgard®. The performance was excellent and the chemicals could be applied during finishing and renewed by the final customer since they could be put into a spray can. However, during the 90's it had become apparent that these materials had spread throughout the global environment and that they were accumulating in biological systems. In 2000, 3M announced that it was ceasing the manufacture of these chemicals and the corresponding products. There is little data on the specific health impact of these chemicals, but the fact that they are found everywhere in everything was cause for concern.

Fluorocarbons can also exist in the form of polymers. These fluoropolymers are not volatile and are even more stable than the small fluorocarbons. The fluoropolymers can have the fluorine attached directly to the chain backbone (like Teflon) or have pendant fluorocarbons groups (telomeric acrylates). They are produced in the form of aqueous dispersions for coating applications. Properly cured coatings, particularly of the telomeric fluoropolymers, can give excellent performance for water, oil and stain resistance. However, concerns have been raised about the use of these fluoropolymers because of the presence of low levels of perfluoroctanoic acid (PFOA) and the potential degradation of the telomeric fluoropolymers to PFOA. For textile purposes, the group of materials related to PFOA are called C8 (There are 8 carbons in PFOA.)

PFOA is another small molecule perfluorocarbon that has numerous uses including use as a surfactant. The method used to synthesize fluoropolymers requires that a surfactant be used to disperse the monomers into tiny droplets in the water. (This kind of system is analogous to the emulsion produced by shaking an oil and water salad dressing to break the oil layer into tiny droplets.) The surfactant is a soap-like material that prevents the polymerization components from separating back into two layers. For fluorine containing monomers, a fluorine containing surfactant is preferred and PFOA works extremely well to produce a stable monomer dispersion which produces a stable fluoropolymer dispersion. This means that the fabric finishing chemicals can form stable coating dispersions.

Manufacturers of fluoropolymers are currently reducing the amount of the PFOA surfactant used, using alternative surfactants, eliminating PFOS as a synthetic contaminant, and removing as much PFOA as possible from the fluoropolymer dispersions. New analytical technology developed by 3M can detect PFOA at a level as low as 1 part per trillion (1 penny in 10 billion dollars) so essentially everything has detectable levels of PFOA. PFOA can be detected at these low levels in finishing solutions containing C8, but there is no evidence to suggest that there is cause for concern at ppt levels.

The degradation issue comes about because while telomeric fluoropolymers are extremely chemically stable, they do degrade very slowly and one of the degradation products is the telomeric fluorocarbon alcohol. When the fluoropolymer uses the $C_8F_{17}CH_2CH_2OH$ (C8-2) starting alcohol, there is evidence that PFOA may be formed due to further degradation.

The fluoropolymer manufacturers have been seeking to incorporate smaller perfluorocarbon segments such as C6 or C4 (analogous to perfluorohexanoic acid (PFHA) or perfluorobutanoic acid (PFBA)) into their polymers so that degradation cannot produce anything as large as PFOA. These smaller fluorocarbons are more rapidly broken down in the environment and more rapidly eliminated from biological systems. Unfortunately, the desired textile performance goes down as the size of the perfluorocarbon goes down.

“C6 is closest chemically to C8, but it contains no PFOA. It breaks down in the environment – a positive trait – but it doesn’t stick as well to outerwear and it doesn’t repel water and oil as well as C8, which means it falls short of meeting a vague industry standard, as well as individual company standards for durability and repellency.” (PFOA Puzzle - Textile Insights -- http://www.textileinsight.com/articles.php?id=37)

Todd Copeland, Patagonia Common Threads material development & environmental assessment of raw materials, agrees. “We haven’t seen anything that has as good performance as C8. We have high standards. If we were to accept a lower level of performance just to get rid of PFOA, I wonder if we’d be doing the right thing or if the environmental impacts of that move would be greater.”

Results with comparable C8 and C6 fluoropolymers indicate that twice as much of the C6 fluoropolymer may be required to give the performance of the C8 fluoropolymer. As a result, it is necessary to coat more C6 containing material to get the same result, so more total fluorochemical is needed.

“We don’t think there is any benefit in making any performance sacrifices or durability compromises,” said Bernhard Kiehl, fabric division sustainability leader, W.L. Gore. “Using a lesser product would result in a negative environmental impact, with more

garments ending up in the landfill, or consumers trying to retreat at home, without the environmental controls of a factory." "DWR manufacturers are cleaning up what they have while developing new product. We're doing the same — working on reducing PFOA across our entire fabric production portfolio, while testing new solutions."

What is happening now:

PFOS and PFOSA are no longer in finishing formulations.

In January 2006, the U.S. Environmental Protection Agency (EPA) approached the eight largest fluorocarbon producers and requested their participation in the 2010/15 PFOA Stewardship Program, and their commitment to reduce PFOA and related chemicals globally in both facility emissions and product content 95 percent by 2010, and 100 percent by 2015.

The fluoropolymer manufacturers are improving their processes and reducing their waste in order to reduce the amount of PFOA materials used. They are investigating smaller perfluorocarbon telomer possibilities but nothing has approached C8 in performance. PFOA is a minor component of telomeric fluoropolymers containing C8. The amount of PFOA in finishing formulations is greatly diminished and continues to go down, but even parts per trillion are detectable. Finishing formulators continue to evaluate new materials which can eliminate PFOA while maintaining performance but a solution is still over the horizon.

But, "The EPA is asking companies to reduce PFOA while simultaneously saying it's nothing to be concerned about." "As the 2010 deadline approaches, the EPA reports that PFOA levels in humans are dropping".

3M stands by its decision to get out of PFOS and PFOA, but their official position is: "In more than 25 years of medical surveillance we have observed no adverse health effects in our employees resulting from their exposure to PFOS or PFOA. This is very important since the level of exposure in the general population is much lower than that of production employees who worked directly with these materials."
- Larry Zobel MD, MPH, 3M Medical Director

The C6/C8 discussion is complex. Eliminating PFOS and reducing PFOA makes sense. At the same time, moving from C8 to C6 may require using 50% more fluorochemical in similar formulations to get the same performance. Therefore, if PFOA can be reduced to extremely low levels (as in GreenShield® C8 formulations), outstanding performance can be obtained at the lowest possible fluorochemical level.