Firefighting foams – Reebok redux

Stephen Korzeniowski (DuPont) and Tom Cortina (Fire Fighting Foam Coalition) reflect on the fluorine-free vs fluorinated foams debate that was brought to the fore during last year's Reebok conference.

Over the past six years, a debate about fluorinated firefighting foams has taken place in a number of venues. Most notable are the three Reebok Stadium meetings held in Bolton, UK between 2002 and 2007. Those who attended these meetings and read the numerous articles in fire industry publications, including the most recent article in the December 2007 issue of IFJ, know that the debate about the efficacy and safety of fluorinated versus fluorine-free fire fighting foams rages on.

In the end, what matters most is the safety and protection of lives and property at risk and the delicate balance of this goal with the potential risk to the environment. The title of the talk presented by one of the co-authors of this article, Dr. Korzeniowski of DuPont, really does get to the heart of the issue: "Safety and protection – be sure."

The presentation clearly showed that science must frame the debate. Not hearsay. Not emotion. In many flammable liquid fires where these agents are used, lives and valuable property are at ultimate risk – complete loss. All chemicals have inherent hazards to people and the environment and may be harmful if not used responsibly. The key is to use the right chemical(s) for the task needed to ensure that what is used is truly the best "fit-for-purpose."

Over the past several years there has been a substantial shift from PFOS-based AFFF agents to equally effective AFFF agents containing fluorotelomer-based surfactants (see figure 1).

With the withdrawal of the PFOS-based products due to their persistence, bioaccumulative and toxic properties (beginning in May 2000) and their subsequent regulation by various national governments, makers of fluorotelomer-based products began more intensive study of the toxicology and environmental fate of their products. Based on the concerns raised by PFOS, Class B agent customers also began to look for fluorine-free alternatives. Both sets of manufacturers – fluorine-based and fluorine-free – have steadfastly maintained that their products are safe and work for their intended uses. However one thing is clear, fluorotelomer-based AFFF surfactants have been tested and shown to be effective in the severest of cases: real and challenging Class B fires.

A primary debate about fluorotelomer-based products centers on the perceived similarity to PFOS, the presence and/or generation of perfluoro-carboxylic acids (PFCAs) such as perfluorooctanoic acid (PFOA), and the ultimate breakdown products of these surfactants. The fate and toxicology of these breakdown products has been brought into full view at the three major Reebok conferences.

First and foremost, fluorotelomer-based surfactants do not contain or degrade to PFOS. They are not made with PFOA or PFCAs. The predominant breakdown product from the six-carbon (C6) based fluorotelomer surfactants (Field 2003) is commonly referred to as the 6:2 fluorotelomer sulfonate (6:2 FtS). They may also contain trace levels of PFOA and the C6 acid, perfluorohexanoic acid (PFHxA). Fluorotelomer producers are working toward the elimination of trace levels of PFOA, PFOA precursors, and related higher homologue chemicals from finished products by 2015 under the US Environmental Protection Agency (EPA) global stewardship program.

The highlighted red box on the left side of Figure 1 calls out the 6:2 FtS structure (where n = 6). Although there have been numerous articles and conference presentations that purport the 6:2 FtS to be a PFOS analog (sometimes incorrectly referred to as H-PFOS), the scientific data do not support this allegation. The physical, chemical, biopersistence and toxicological properties of 6:2 FtS are not similar to PFOS.

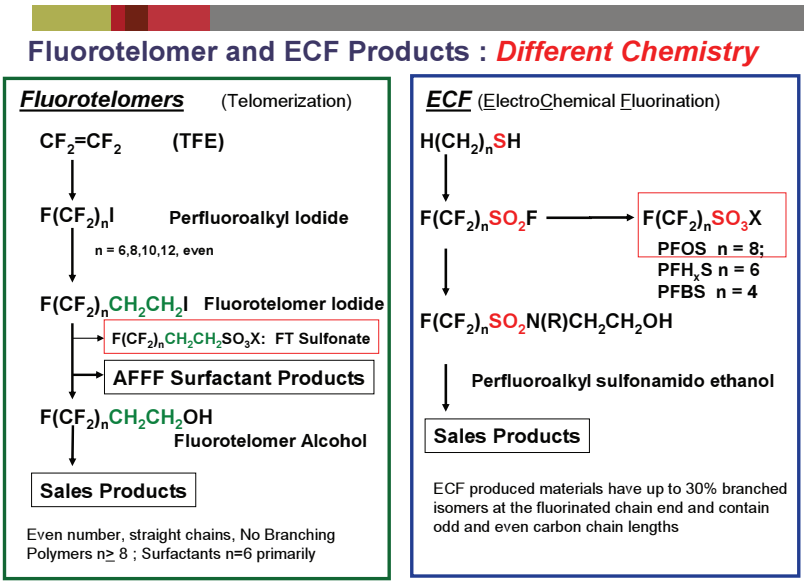


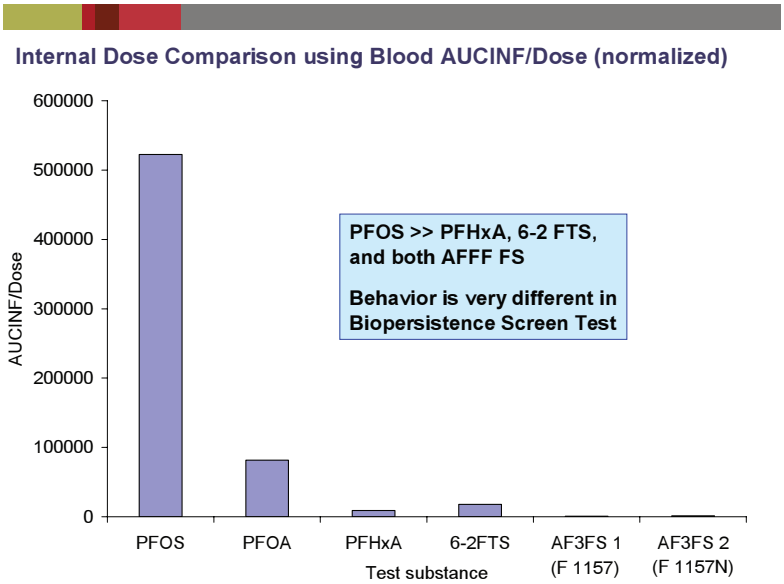
Figure 1; comparison between fluorotelomer-based and PFOS-based chemistry.

Biopersistence

The results of a 6:2 FtS biopersistence screening study were presented at the September 2007 Reebok conference. The data presented are shown in Figure 2 (publication in preparation). This screening study involves oral dosing of male rats for 10 days followed by an 84-day recovery period. The study determined total organic fluorine levels in plasma, liver, and fat. It provides a screening measure of what toxicologists refer to as biouptake and bioclearance. The AUCINF, or area under the curve integrated to infinity, provides a relative integrated measure of the absorbed dose of the compound studied. A compound that is absorbed and quickly eliminated or is simply not absorbed will have a low relative AUCINF. It is very clear from Figure 2 that the 6:2 FtS, the C6 acid (PFHxA), and the two commercial fluorotelomer-based firefighting surfactants have extremely low values when compared to PFOS. In this study, PFOA is also lower when compared to PFOS.

Toxicology (aka "hazard")

A second part of the debate seems to focus on the potential hazards of PFHxA and the 6:2 FtS. These two compounds can be both contaminants in the final products as well as potential degradants once the AFFF agents are used. The debate however has



no place for innuendo and must be based on real hazard data. Extensive data on PFHxA were presented at the US EPA PFOA Information Forum in June 2006 that gave a very favorable initial toxicology (hazard) profile (AGC Chemicals, Asahi Glass, 6/8/06). Additional information was presented at the September 2007 Reebok conference that further supported the favorable toxicology profile of PFHxA. Preliminary data were shared on four major toxicology end points: sub-chronic toxicity in rats, reproductive toxicity in rats, developmental toxicity in rats, and genetic toxicity. It was noted at this conference that PFHxA was neither a selective reproductive nor a selective developmental toxicant. In addition it was clearly shown to be neither genotoxic nor mutagenic. Combining these data with those presented in June 2006 provides significant evidence that this particular end product has a low hazard profile based on current data.

Based on recent groundwater studies (Field 2003), the 6:2 FtS has been shown to be the likely ultimate degradation product of the fluorotelomer-based surfactants used in today's AFFF agents. The screening study cited above (Figure 2) indicated that the 6:2 FtS had a low relative biopersistence potential. The 6:2 FtS had a high NOEC (no observed effect concentration) in the 90-day early life stage trout study. Results presented at the Reebok conference in September 2007 provided preliminary new results on environmental effects as well as bioconcentration (BCF) and bioaccumulation (BAF) in rainbow trout. Although the data were preliminary in nature, the results were clear and compelling. Moreover both the BCF and the BAF values suggest low concern for bioaccumulation from water or diet. The data strongly suggested that 6:2 FtS is not bioaccumulative according to published regulatory criteria and affirmed that it doesn't behave like PFOS.

Conclusion

Firefighting foams that contain fluorotelomer surfactants stand on a substantial foundation of scientific data. They are the most effective agents currently available to fight flammable liquid fires and are safe for their intended uses in military, industrial, and municipal settings. The suggestion that fluorine-free alternatives are safer and environmentally superior is simply not based on available science, and certainly not based on the information presented at the Reebok conferences.