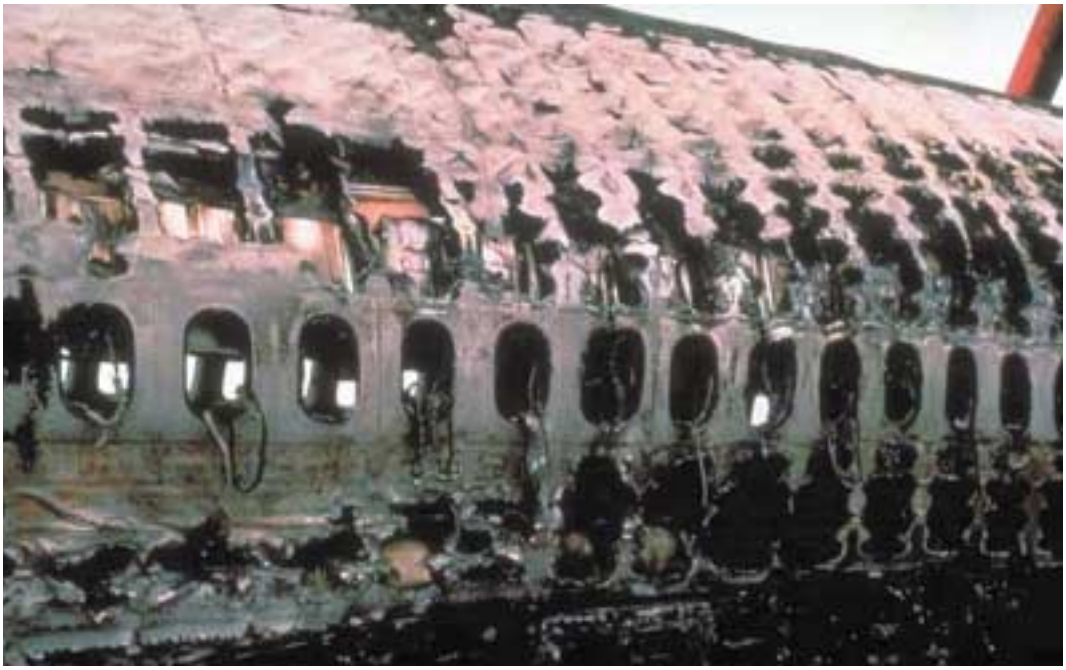

The Phaseout that Didn't Happen

AFFF Foams Move into the Future

It has been ten years since 3M sent a shock wave through the fire protection industry with their announcement that they would end production of PFOS-based AFFF foams because of environmental issues with the fluorosurfactants they contained. This is also about the time that many so-called "experts" said that all AFFF foams would be phased out of production for similar environmental reasons. Instead, telomer-based AFFF foams continue to be the agent of choice to protect against flammable liquid fires, and manufacturers have developed enhanced foam formulations with reduced environmental impacts that can be used well into the future. Why were the experts wrong in their predictions?

By Tom Cortina

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Halon experience colors industry view

Part of the reason for the speculation about a possible phaseout of AFFF foam after the 3M announcement was that at the time, the fire protection industry's only real experience with environmental regulation was the phaseout of halons as ozone-depleting substances. Based on this experience many people in the industry assumed that this is how environmental regulation works; a chemical is determined to have some negative impact and is banned from future production. In reality, however, the phaseout of ozone-depleting substances was a unique situation. Most environmental regulation focuses on the toxicity of a substance and has the goals of reducing emissions to the environment and exposure to humans. Very rarely are chemicals actually banned from production. For ozone-depleting substances, the focus was atmospheric effects and it was determined that the only way for the ozone layer to recover fully was to end the worldwide production of these chemicals.

The other reason for speculating about a possible phaseout of AFFF was business related. Companies selling non-fluorosurfactant foams saw an opportunity to use the negative publicity surrounding the 3M announcement as a way to enhance sales of these less effective alternatives. Unfortunately that practice continues today, even though it seems clear that global regulation of AFFF is not on the horizon. We continue to see articles in fire protection journals from manufacturers of fluorine-free foams that contain misleading and in some cases false information about the environmental impacts and future regulation of AFFF. The strange thing about this situation is that many of these same companies also sell AFFF. If they actually believe what they write in these articles, that

fluorosurfactant foams are not safe for the environment, why do they continue to sell the products?

Focus on fluorosurfactants

Historically, most of the environmental concern related to fire fighting foams has focused on aquatic toxicity and residual foaming, which can be a concern for local waterways and sewage treatment systems, and are common problems for all foams[1]. Starting about ten years ago the focus shifted to the fluorosurfactants that are a key ingredient in aqueous film-forming foams (AFFF). Fluorosurfactants provide AFFF with the required low surface tension and positive spreading coefficient that enables film formation on top of lighter fuels. It is this film formation capability that gives AFFF its name and its effectiveness against flammable liquid fires. AFFF agents provide rapid extinguishment, burnback resistance, and protection against vapor release.

Fluorosurfactants and related fluorochemical polymers are used in many applications besides fire fighting foams including paper and packaging, textiles, leather and carpet treatment, and coatings. Some of these fluorochemicals and/or their persistent degradation products have been found in living organisms, which has drawn the concern of environmental authorities worldwide and led to both regulatory and non-regulatory actions to reduce emissions. The focus of these actions has been on fluorochemicals that contain eight carbons (C8) or more such as PFOS (perfluorooctane sulfonate) and PFOA (perfluorooctanoic acid).

3M used a unique process to manufacture the fluorochemical surfactants contained in its fire fighting foams. This process is called electrochemical fluorination (ECF), and fluorochemicals produced by this process both contain and degrade into PFOS. 3M stopped the manufacture of PFOS-based foams in 2002, and regulations in the United States (US), Canada, and the European Union (EU) act as a ban on new production. EPA regulations do not restrict the use of old stocks of PFOS foam in the US. Regulations in the EU and Canada require old stocks of PFOS foam to be removed from service in 2011 and 2013, respectively. Excess stocks of PFOS foam concentrate can be destroyed by high temperature incineration at any approved hazardous waste destruction facility for a relatively low cost.

All current manufacturers in the US and Europe use a process called telomerization to produce the fluorosurfactants contained in their fire fighting foams. Chemicals produced by this process are generally referred to as telomers. Telomer-based foams do not contain or degrade into PFOS. They are not made with PFOA, but may contain trace levels as a contaminant of the manufacturing process. It should be noted that there is continued production of PFOS-based materials for AFFF applications in China despite the restrictions in other regions of the world.

Global stewardship approach

Rather than regulate emissions of PFOA, the US Environmental Protection Agency (EPA) developed a global stewardship program that has been adopted by other countries such as Canada. Under the program eight fluorochemical manufacturers have voluntarily agreed to reduce 95% by year-end 2010 and work to eliminate by year-end 2015 both plant emissions and product content of PFOA, PFOA precursors, and related higher homologue chemicals. As a result, telomer-based fluorochemicals that are used in fire fighting foams are likely to transition to only six carbons (C6) or fewer in order to comply with the global stewardship program. This will require some reformulation and likely some type of re-approval of most current AFFF, FP, and FFFP foam products between 2010 and 2015. There are telomer-based AFFF agents that have been on the market for decades that contain greater than 95% C6 fluorosurfactants and meet the world's most challenging foam standards, so manufacturers are confident that the new products will retain all of the same fire suppression capabilities as existing AFFF agents.

Environmental update

Over the past several years makers of telomer-based products, not surprisingly, have undertaken more intensive study of the toxicology and environmental fate of their products. For AFFF this research has focused on the predominant breakdown product of the C6 fluorosurfactants they contain, which is commonly referred to as the 6:2 fluorotelomer sulfonate (6:2 FTS)[2]. Although there have been articles and conference presentations that claim the 6:2 FTS to be a PFOS analog, the scientific data do not support this allegation. A broad range of existing data indicate that 6:2 FTS is not similar to PFOS in either its physical or ecotoxicological properties[3,4,5,6]. Recent studies on AFFF fluorosurfactants likely to break down to 6:2 FTS show it to be generally low in acute, subchronic, and aquatic toxicity, and neither a genetic nor developmental toxicant. Both the AFFF fluorosurfactant and 6:2 FTS were significantly lower than PFOS when tested in biopersistence screening studies that provide a relative measure of biouptake and clearance[7]. Aerobic biodegradation studies of 6:2 FTS in activated sludge have been conducted to better understand its environmental

fate. Preliminary results were reported at the Reebok foam conference in July 2009 and a publication is in preparation[8].

Work has also been done on a possible contaminant that may be found in trace quantities in AFFF-type fluorosurfactants: perfluorohexanoic acid (PFHxA). Extensive data on PFHxA were presented at an EPA PFOA Information Forum in June 2006 that gave a very favorable initial toxicology (hazard) profile [9,10]. Additional information was presented in September 2007 at a major foam conference in the UK (Reebok) that further supported the favorable toxicology profile of PFHxA[11]. 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.

Fluorine-free foams

Foam manufacturers continue to evaluate many types of potential products that do not contain fluorosurfactants, but efforts to date have not yielded working products with fire performance across all fuels and in all operational circumstances equal to film-forming foams. Some fluorine-free foams can provide an alternative to AFFF in some applications, but they are not currently able to provide the same level of fire suppression capability, flexibility, and scope of usage. A recent paper from the University of Newcastle shows that standard AFFF foam can suppress n-heptane vapor for 140 minutes, while the best available fluorine-free foam under the same conditions held for only 60 minutes[12].

Fluorine-free foams are often championed as "environmentally-friendly" alternatives to AFFF. Although such foams may not contain fluorine, their environmental profile related to biodegradation, acute toxicity, chemical oxygen demand (COD), and biochemical oxygen demand (BOD) is typically no better than fluorine-containing products and in many cases is not as environmentally responsible in use as AFFF. A recent study of commercially available fire fighting foam agents indicates that fluorine-free foams are at least an order of magnitude higher in aquatic toxicity than AFFF agents[13].

Moving forward

AFFF and fluorochemical manufacturers have worked closely with environmental authorities over the past decade, and are currently doing the research and testing necessary to incorporate into their AFFF formulations the new fluorochemicals that are being developed to comply with global stewardship programs. This work will ensure that safe and effective AFFF agents that meet new and challenging environmental requirements will continue to be available to fight flammable liquid fires in military, aircraft, industrial, and municipal settings. IFP

References

[1] Environmental Impacts of Fire Fighting Foams by William H. Rupert, Daniel P. Verdonik, and Christopher Hanauska of Hughes Associates, Inc. (2005)

[2] Quantitative Determination of Fluorotelomer Sulfonates in Groundwater by LC MS/MS, Melissa M. Schultz, Douglas F. Barofsky and Jennifer Field, Environmental. Sci. Technol. 2004, 38, 1828-1835

[3] DuPont 2007a. H-27901: Static, Acute 96-Hour Toxicity Test with Rainbow Trout, *Oncorhynchus mykiss*. Unpublished report, DuPont-21909.

[4] DuPont 2007b. H-27901: Static, Acute 48-Hour Toxicity Test with *Daphnia magna*. Unpublished report, DuPont-21910

[5] DuPont 2007c. H-27901: Static, 72-Hour Growth Inhibition Toxicity Test with the Green Alga, *Pseudokirchneriella subcapitata*. Unpublished report, DuPont-22048.

[6] DuPont 2007d. H-27901: Early Life-Stage Toxicity to the Rainbow Trout, *Oncorhynchus mykiss*. Unpublished report, DuPont 22219.

[7] Serex, T. et al, 2008. Evaluation of Biopersistence Potential Among Classes of Polyfluorinated Chemicals using a Mammalian Screening Method. SOT 2008 Poster #958

[8] Aerobic biodegradation studies of 6:2 fluorotelomer sulfonate in activated sludge, N. Wang et al, DuPont, manuscript in preparation, 2010

[9] Chengalis, C.P., Kirkpatrick, J.B., Radovsky, A., Shinohara, M., 2009a A 90-day repeated dose oral gavage toxicity study of perfluorohexanoic acid (PFHxA) in rats (with functional observational battery and motor activity determinations). Reprod. Toxicol. 27, 342-351.

[10] Chengalis, C.P., Kirkpatrick, J.B., Myers, N.R., Shinohara, M., Stetson, P.I., Sved, D.W., 2009b Comparison of the toxicokinetic behavior of perfluorohexanoic acid (PFHxA) and nonafluorobutane -1-sulfonic acid (PFBS) in monkeys and rats. Reprod. Toxicol. 27, 400-406.

[11] Loveless, S.E., Slezak, B., Serex, T., Lewis, J., Mukerji, P., O'Connor, J.C., Donner, E.M., Frame, S.R., Korzeniowski, S.H., Buck, R.C., Toxicological evaluation of sodium perfluorohexanoate. Toxicology 264 (2009) 32–44.

[12] Schaefer T.H., Dlugogorski B.Z. and Kennedy E. M., "Vapour suppression of n-heptane with fire fighting foams using laboratory flux chamber", 7th Asia-Oceania Symp. Fire Scie. Tech. (in review).

[13] 96-hour LC50 Value in Fathead Minnows (flow-through test), Report of tests on six fire fighting foam agents performed by Aqua Survey Inc., Flemington, New Jersey, USA and 96-hour LC50 Test in Fingerling Rainbow Trout, Report of tests on six fire fighting foams agents performed by Harris Industrial Testing Service Ltd., Nova Scotia, Canada