AFFF – The Most Effective Agents

“Aqueous film-forming foams (AFFF) are the most effective agents currently available to fight hydrocarbon fuel fires in military, industrial, and municipal settings.”

This is not an opinion, but a statement of fact that is not disputed by any respected fire protection professional. It has been consistently proven in fire tests done over the last 30 years and in tests that are being performed today.

Despite this fact, a number of articles have been published in the last few years in fire protection journals that suggest using less effective agents. The basis for these suggestions is environmental concerns about the fluorinated surfactants contained in AFFF. But there are two different kinds of AFFF that have been produced over the past 25 years and they contain different types of fluorinated surfactants that have different environmental properties. Many of these articles appear to blur the distinctions between the different types of AFFF so the authors can speculate about environmental and regulatory controls that are not and have never been seriously considered. Before you make a decision to use a less effective agent to protect lives and critical facilities, make sure you know all the facts.

Fluorinated Surfactants

All AFFF fire-fighting agents contain fluorinated surfactants (fluorosurfactants). They are a key ingredient that provides 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.

3M used a unique process to manufacture the chemical components of the fluorosurfactants contained in its AFFF formulations. The process is called electrochemical fluorination (ECF), and fluorosurfactants produced by this process both contain and degrade into chemicals known as PFOS (perfluorooctyl sulfonate) and PFOA (perfluorooctanoic acid). The U.S. Environmental Protection Agency (EPA) has classified PFOS as persistent, bioaccumulative, and toxic (PBT).

All other manufacturers use a process called telomerization to produce the chemical components of the fluorosurfactants contained in their AFFF. Chemicals produced by this process are generally referred to as telomers. Telomer-based AFFF agents do not contain or degrade into PFOS.

EPA Workgroup Determines AFFF Not a Likely Source of PFOA

Ever since 3M announced its decision to end production of AFFF there has been intense speculation, fueled by a variety of interest groups, that other AFFF agents would also eventually disappear. This speculation was based largely on the belief that telomer-based AFFF agents could break down in the environment into perfluorooctanoic acid (PFOA), and that sources of PFOA would eventually be regulated as have sources of PFOS. In October 2003, however, an EPA workgroup determined that telomer-based AFFF is not likely to be a source of PFOA in the environment. EPA concluded that existing data “provided no evidence that these fluorosurfactants biodegrade into PFOA or its homologs…”

The decision of the EPA Telomer Technical Workgroup (10/29/03) was based in part on the following information:

- Telomer-based AFFF agents are not made with PFOA and contain no PFOA-based products.
- PFOA is an eight-carbon molecule (C₈). The majority (over 80%) of the fluorosurfactants used in telomer-based AFFF are derived from six-carbon perfluoroalkyl molecules (C₆). There is no known pathway for the C₆ fluorosurfactants used in AFFF to break down into PFOA.

Another influence in the EPA workgroup decision was a report by Dr. Jennifer Field of Oregon State University that contained data on fluorosurfactants in groundwater at three
military sites where AFFF was used to train fire responders (7/3/03, EPA docket number OPPT-2003-0012-0144). A variety of fluorinated chemicals were found in groundwater at each location. She broke the fluorinated chemicals into three classes: perfluorooalkyl sulfonates, which include PFOS; perfluorooalkyl carboxylates, which include PFOA; and telomer sulfonates. Perfluorooalkyl sulfonates ranging from four to eight carbons and perfluorooalkyl carboxylates ranging from six to eight carbons were found at all three locations. Telomer sulfonates, 97-99% with six carbons, were found at two of the three locations.

**Telomer Breakdown**

Dr. Field concluded that the perfluorooalkyl sulfonates and perfluorooalkyl carboxylates came from ECF-based AFFF agents and that the telomer sulfonates came from telomer-based AFFF agents. (Similarly, based on their knowledge of the exact chemistry of the telomer-based AFFF agents sold to the military, industry scientists have concluded that the telomer sulfonates found in the groundwater on military bases are the likely biodegradation product of the fluorosurfactant active ingredients in AFFF.) Dr. Field also concluded that there was no evidence from this study that telomer sulfonates were breaking down in the groundwater into perfluorooalkyl carboxylates. Statements in recent articles that there is a correlation in the Field study between the presence of telomer sulfonates and perfluorooalkyl carboxylates are in direct conflict with the conclusions of the author that “no correlation appears to exist between the occurrence and concentration of telomer sulfonates and perfluorooalkyl carboxylates in the AFFF-contaminated groundwater sample set.”

In fact, the opposite appears to be true. Groundwater from wells that were 500 meters from the fire training area at one site contained 6:2 telomer sulfonates, but the corresponding six-carbon perfluorooalkyl carboxylates were not found. That the 6:2 telomer sulfonates had been in the groundwater for at least 10 years and no corresponding six-carbon perfluorooalkyl carboxylates were found indicates that telomer sulfonates do not biodegrade to perfluorooalkyl carboxylates under these groundwater conditions.

**6:2 Telomer Sulfonate is Not Similar to PFOS**

There have also been statements in some recent articles insinuating that the 6:2 telomer sulfonate (6:2 FTS) is somehow similar to PFOS in terms of chemical structure, biological toxicity and bioaccumulation. This is simply not true. Each of these compounds should be evaluated on its properties. It is unacceptable to make sweeping generalizations in the absence of data.

The 6:2 FTS has six fluorinated carbons, not eight like PFOS. It is not fully fluorinated as it has an ethylene spacer between the fluorocarbon chain and the functional end group. These two elements alone provide some very significant differences in chemical properties. AFFF agents containing the 6:2 FTS backbone as well as derivatives used as surfactants for other applications have been studied. Results from these studies will be reported at the NFPA World Safety Conference and Exposition in June.

**Inventory Study**

One of the conclusions that can be drawn from the Field report is that the presence of PFOS and PFOA from fire fighting foams currently in the environment is a legacy issue associated with the historical use of ECF-based AFFF. In order to get a handle on how much ECF-based AFFF remains in the field, EPA asked the Fire Fighting Foam Coalition (FFFC) to study inventories of ECF-based and telomer-based AFFF. FFFC recently submitted a report to EPA of an independent study that estimates that there are about 10 million gallons of AFFF in inventory in the United States. About 45% of this is ECF-based product (3M) and about 55% is telomer-based product. The major users of AFFF based on inventory are the military, refineries and other petrochemical facilities, aviation (ARFF and hangars), and municipal (fire departments).

Current EPA policy is to prohibit production of new products containing PFOS, but it does not restrict use of existing stocks of PFOS-based products. Whether and to what extent EPA will take action in response to the inventory data is not clear at this time.

**Fluorine-Free Foams**

Foam manufacturers continue to evaluate products that do not contain fluorosurfactants, but it should be noted that efforts to date have not proven to yield working products with fire performance equal to film-forming foams. Such fluorine-free foams may provide an alternative to AFFF for some applications, but they are not currently able to provide the same level of fire suppression capability, flexibility, scope of usage, and independent validation.

Fluorine-free products have existed for many years, including high expansion, medium expansion, and basic protein foam concentrates. Although these products do not contain fluorosurfactants, their environmental profile related to biodegradation, acute toxicity, chemical oxygen demand (COD), and biochemical oxygen demand (BOD) is generally no better than fluorine-containing products and in many cases is not as environmentally friendly as AFFF. In addition, alternative products typically require higher application rates for control and extinguishment, resulting in higher costs for water supplies, system installations, pumping systems, and ultimately for containment and disposal costs where required.

The fluorosurfactants contained in many modern, telomer-based AFFF solutions account for less than 0.1% of the solution. This is because the surfactants are extremely effective in reducing surface tension and improving spreading over the fuel surface. Very little surfactant is needed to create a product that provides the highest level of fire performance and personnel safety. ■