# MISCELLANEOUS

## *TECHNICAL BULLETIN BUCKEYE FIRE FIGHTING FOAM PRODUCTS AND THE ENVIRONMENT*

### FOAM BIODEGRADATION IN THE ENVIRONMENT

Because of the widespread use of fire fighting foam concentrates, there exists the potential for a large release of this material into the environment. Although this is a small risk, it is important to ensure that these products are as safe for the environment as possible.

With increasing awareness and corporate responsibility from the Fortune 500 companies, the indiscriminate discharge of fire extinguishing media to the environment has been greatly reduced. There are however periodic discharges of fire protection systems and these could be classified, or fall into two (2) categories; accidental and deliberate. In other words, a system could discharge as a result of a malfunction, in for example a detection system, thus producing an "unwanted" discharge. Then there is the deliberate or planned activation of a system for test purposes, or the designed activation in the event of a fire. The later two examples are "wanted" discharges. In either case though, extinguishing media has been discharged into the environment.

Buckeye Foam Concentrate formulations are configured for as rapid degradation as possible, thereby preventing surfactant buildup and accumulation in the environment. Biodegradation is a key element in reducing the environmental load or burden associated with the high volume use of surfactant chemicals.

There are effectively seven factors when considering the environmental impact of foam concentrates and all of these factors are of concern when the end-use foam solutions reach natural or domestic water systems. These factors are: 1). Fluorochemicals, 2). Fish Toxicity, 3). Biodegradability, 4). Sewage Treatment Plant Treatability, 5). Nitrogen, 6). Phosphates, 7). Heavy Metals. To determine the effect that the foam concentrates might have on the environment, they are subjected to a series of tests. To ensure accurate, repetitive and un-compromised data for use by commercial & governmental organizations, an independent laboratory performs the majority of these tests.

**In the early 1990's a solvent called butyl carbitol (diethylene glycol butyl ether {DGBE}) was used as a foam enhancer in most aqueous film forming foam (A.F.F.F.) concentrates. This material subsequently found it's way on to the Federal Register of Hazardous Air Pollutants. Thus every time this material was released to the environment, including that contained in the A.F.F.F. products, it was necessary to report that "spill" to the Environmental Protection Agency (E.P.A.). Some of the A.F.F.F. manufacturers responded by re-formulating their products to remove the butyl carbitol. Buckeye was one of those manufacturers and we took a corporate responsibility to make our A.F.F.F. products as "Environmentally Friendly" as possible, while still maintaining the highest level of fire fighting performance.**

### FLUOROCHEMICALS

During May of 2000, The 3M Company decided to discontinue its A.F.F.F. product line with the effective end of production occurring sometime around November 2001. The reason for this withdrawal was based on test results that determined a base material used in the production process (perfluorooctyl sulfonate) is considered P-B-T (Persistent, Bio-accumulative & Toxic) and as such further use would be harmful to the environment. It is very important to state that the major contributor to fluorochemical build-up in the environment is not by fire fighting foam concentrates but by the 3M-fabric protectorant, Scotchgard® and other complimentary products used to protect food-wrapping paper. In fact, fire fighting foam concentrates represent less than 2% of the fluorochemical use, worldwide. There is no doubt that these fluorochemicals are long lasting and the announcement by 3M has highlighted this issue. Foam concentrates manufactured by Buckeye DO NOT CONTAIN (PFOS), the P-B-T fluorochemical used in manufacturing the 3M product. For the foreseeable future, we expect A.F.F.F. concentrates to be freely available, since they are considered "essential" products for life safety.

#### Fluorinated Surfactants

All A.F.F.F. fire-fighting agents, (standard and alcohol resistant), along with the fluoroprotein and film forming fluoroprotein (F.F.F.P.) foam concentrates contain fluorinated surfactants. They are a key ingredient, which provides these agents with the required low

surface tension (15 to 17 dynes/cm) and positive spreading coefficient that enables film formation on top of most hydrocarbon fuels. The chemicals used to produce fluorinated surfactants can be manufactured by different processes and have different chemical structures. The fluorinated surfactants used in A.F.F.F. are produced from fluorochemicals manufactured by two methods: electrochemical fluorination and telomerization.

**Electrochemical Fluorination**
The key fluorochemical raw material produced by electrochemical fluorination is perfluorooctane sulfonyl fluoride (POSF). POSF has been produced since the 1950s for the synthesis of fluorochemicals used in paper and packaging; textile, leather, and carpet treatment; industrial surfactants, additives, and coatings; and surfactants in fire fighting foam agents such as A.F.F.F. The degradation of POSF-derived fluorochemicals as well as the hydrolysis or neutralization of POSF results in the formation of perfluorooctyl sulfonate (PFOS). PFOS is currently a major focus of the U.S. EPA's regulatory activities.

**PFOS - What are the issues?**
The EPA has published a hazard assessment (not a risk assessment) that categorizes PFOS as P-B-T:

P = persistent
B = bio-accumulative
T = toxic

PFOS has been found in the blood of workers handling the chemical, the general U.S. population, people in other developed countries, and in wild birds and fish. Levels detected in workers were as high as 12 parts per million (ppm) and levels detected in the general population were in the 30-50 parts per billion (ppb) range.

**PFOS - How big a risk is it?**
The EPA does not believe that the current situation presents an imminent health risk to the general population, but the EPA has concern for potential future risk if PFOS continues to be produced and released to the environment. The EPA has questions and concerns about occupational exposures to PFOS.

**PFOS - What is being done?**
3M will voluntarily phase out manufacture of POSF-derived fluorochemicals for use in performance products (which includes Light-Wate® A.F.F.F.) by December 31, 2002. (A.F.F.F. concentrate production ceased prior to this date). The EPA has proposed a Significant New Use Rule (SNUR) that is intended to "close the door" on future manufacture and import of POSF-derived fluorochemicals as well as PFOS.

**Impact of The EPA's Actions**
The EPA's initial actions and 3M's phase out apply only to PFOS and its derivatives. Telomer-based A.F.F.F. will continue to be produced and no disruption of supplies will or has been experienced. The EPA is currently assessing other perfluorinated chemicals like PFOA and related chemistries such as telomer products (see below). Telomer-based A.F.F.F. does not contain PFOS or any other compound currently considered by regulatory agencies to be P-B-T. There is no known biological pathway by which telomer-based A.F.F.F. can be oxidized or metabolized into PFOS. Telomer-based A.F.F.F. agents contain 30-60% less fluorine than A.F.F.F. based on POSF-derived fluorosurfactants.

**Perfluorooctanoic Acid (PFOA)**
The predominant production of PFOA is also by the electrochemical fluorination process. The EPA is currently assessing the hazard of PFOA and expects to publish a hazard assessment sometime before mid - 2002. PFOA is known to be persistent, and substantial toxicity data on PFOA exists in public literature and regulatory agency files. Telomer-based A.F.F.F. is not made from PFOA-based products.

**Telomers**
Telomers is a term used to describe the most common synthetic route for manufacturing perfluoroalkyl compounds that have straight chains of 6-14 carbons. The fluorochemical portion of telomer molecules is persistent, but preliminary data on toxicity and bioaccumulation indicate that telomers are very different when compared to PFOS. In order to better understand the potential environmental effects of telomers, the manufacturers have begun a voluntary research program, the results of which will be shared with the EPA and others. The EPA will be assessing the environmental hazard presented by telomers over the next few years based on existing data and new data generated by the TRP (Telomer Research Program) and elsewhere.

**Telomer Research Program (TRP)**
The TRP is a science-focused research consortium funded by global fluorotelomer manufacturers. The TRP is conducting a 2-3 year research program on common raw material: Telomer 8-2 alcohol. The testing program includes studies on pharmacokinetics (how the compound is metabolized), environmental fate and effects (what does the compound break down

into in the environment and what are the effects) and toxicity.

**A.F.F.F. Manufacturers**
What are A.F.F.F. manufacturers doing to address the environmental concerns about A.F.F.F.? A.F.F.F. manufacturers, in conjunction with fluorosurfactant manufacturers and telomer producers, have formed the Fire Fighting Foam Coalition (FFFC). The founding members of FFFC include, Buckeye, Ato-Fina, Dupont, Dynax, and other foam concentrate manufacturers. FFFC was formed to represent the A.F.F.F. industry's interests on all issues related to the environmental acceptability of fire fighting foams. The coalition provides a focal point for industry science reviews, development of industry positions, and interactions with the EPA and other relevant organizations.

## FISH TOXICITY

Foam solution "run-off" is always a concern in fire-fighting operations, since that "run-off" could work it's way into streams, rivers and the ocean. However, it is also important to consider the fuel involved in the fire, which when spilled can also present a potentially larger problem in terms of aquatic toxicity, than the foam/water solutions. Fish are relatively sensitive to the presence of pollutants in the water and as such, foam solutions are tested to determine fish toxicity. These tests are normally run on both estuarine and fresh water species, with the two most common test species being the Killifish and the Rainbow Trout. The Killifish is tolerant while the Rainbow Trout is sensitive. The tests on these two species gives an indication of the broad range over which various fish populations may be affected. The results are given as the 96-hour LC/50, a measurement of the concentration lethal to 50 percent of the test population, during a 96-hour period. The units of measure are milligrams/liter or parts per million (ppm). The higher the values on the test, the greater the tolerance of the fish to the Buckeye Foam Products. For Rainbow Trout we found that the test 96 LC/50 values range from 4,500 to 7,000 ppm while Killifish have a 96 LC/50 range from 25,000 to 37,000 ppm. There is some debate as to the exact reason the fish die; in some cases, it may not be a chemical effect from the foam concentrate, but rather an inability of the fish to "breathe" as a result of oxygen depletion in the water. Based on the test results, fish toxicity is not of particular concern for the synthetic foam concentrates.

## BIODEGRADABILITY

The biodegradability of Buckeye foam solutions is dependent on a number of factors. For example: the amount of dilution that occurs prior to a release and the area in which the release occurs. To determine the biodegradability of these solutions two tests are conducted and a relationship between the two results developed. The two tests are BOD (Biological Oxygen Demand) (oxygen demand by the microorganisms) and COD (Chemical Oxygen Demand) (oxygen used in chemical decomposition). COD measures how much oxygen would be required to completely break down the chemicals contained in the foam solution. BOD then measures how much oxygen the bacteria will consume as they use up ("eat") the chemicals found in a given amount of foam solution. For an A.F.F.F., the BOD test is carried out over a 20-day cycle. Since most foam solutions have a BOD/COD over 0.5 or 50% they are considered relatively biodegradable.

## SEWAGE TREATMENT PLANT TREATABILITY

Buckeye foam products are not particularly toxic to the ultramicroscopic size organisms found in water treatment plants. For water treatment plants that use the activated sludge process for secondary treatment, Buckeye Foam Concentrates may cause foaming, the foam could then carry over (and out of the plant) suspended solids and consequently, a large amount of the microbial population, reducing the effectiveness of the plant. Solutions of Buckeye foam products, up to 300 ppm can typically be handled without adverse effects. For the most part, the dilution, which takes place on the way to the water treatment plant, brings the concentration down below the 250-ppm level. If it does not, the use of a de-foaming agent such as Dimethylpolysiloxane, Dow Corning H-10, DB 110A, 1410 or Henkel WB-209, which are compatible with the treatment plant's flora, may allow handling of concentrations above the 300-ppm level.

## NITROGEN

Some of the surfactants used in synthetic foam concentrates may contain small amounts of nitrogen in an organic form, however, the level is relatively low and little environmental impact can be expected.

The protein based foam concentrates contain substantially more organic nitrogen than synthetic foam concentrates and will act as very effective fertilizers promoting excessive growth of plants and algae in waterways.

## PHOSPHATES

It is remotely possible that some cheaper foam compounds could contain phosphates. Phosphates act as fertilizers and will promote excessive growth of some

plants and algae. Discharging phosphates into a body of water can damage the ecology by promoting excessive plant growth along the banks that could block waterways. Buckeye Fire Fighting Foam Concentrates do not contain phosphates.

**HEAVY METALS**

Heavy metal ions such as zinc can be found in some protein foam concentrates and could accumulate in living organisms, which can be harmful. Releasing heavy metals to the environment should be avoided whenever possible.

**CURRENT POSITION**

Early on, Buckeye took a position to produce foam concentrates with the lowest possible environmental impact and the highest possible fire fighting effectiveness. The world is becoming smaller and more aware of the impact associated with the chemicals we use in our everyday operations. Anything not of a naturally occurring substance, such as man-made chemicals are likely to be undesirable for the environment and discharges should be limited.

Buckeye formulates Earth Friendly Foam Concentrates without DGBE. This decision was based on information generated from the market place, with origins dating back to 1993. As a result of a ruling by the E.P.A. (Environmental Protection Agency) in 1993, A.F.F.F. concentrate or A.F.F.F. solution discharges became a reportable incident under EPCRA, (Emergency Planning and Community Right-to-Know Act), SARA Title III. This was because the majority of these foam concentrates contained the glycol ether called butyl carbitol or DGBE. The glycol ether is or was used as a 'foam-enhancer' to improve the foamability, increase burnback resistance and produce rapid knockdown capabilities. Once one (1) pound (0.45 kg) of glycol ether was spilled, (this represents approximately one [1] gallon or 3.8 litres of foam concentrate), it was considered a reportable incident, since this material was listed on the Federal Register as a toxic hazardous material; specifically a hazardous air pollutant.

In 1996 the reporting procedures for A.F.F.F. foam/water solution discharges containing glycol ether were lifted and now there are no minimum reportable quantities. However, even though it is not now necessary to report these discharges, the owner is still responsible for proper clean-up and disposal of any foam/water solution containing glycol ether. It therefore makes environmental and commercial sense to use A.F.F.F. concentrates that do not contain glycol ether.

Thus foam concentrates offering the lowest environmental impact should be chosen over those with higher environmental impact.

To further reduce environmental impact Buckeye offers an environmentally benign, non-foaming agent that can be used for testing foam systems. This agent mimics exactly, the "real" foam concentrate and simulates the performance of the system to verify proportioning accuracy. Additional information on this innovative method is available from the Buckeye Foam Systems Engineering Department.

Trying to determine the foam concentrate demonstrating the lowest environmental impact is a difficult task. This is made more complex due to a lack of complete and accurate information. Any claim that a regular protein based foam concentrate has lower environmental impact than a fluorosurfactant based foam concentrate cannot be substantiated. These two types of foam concentrate affect the environment in different ways, but neither can be shown better or worse than the other. Thus proper evaluation of the M.S.D.S. (Material Safety Date Sheet) should be exercised and the appropriate decision made.

Buckeye has a Technical Support Department that can provide additional information and updates to these very important environmental issues.