Fluorotelomer Based Foams:

Are They Safe For Continued Use?

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It is now almost 10 years since PFOS was first accepted as a Persistent, Bioaccumulative and Toxic ingredient in certain detergent based foam concentrates, and started being phased out of production and use in all firefighting foams. Firefighters around the world have still been unsure whether the telomer based alternatives are safe for continued use, or whether they are better accepting the limitations of fluorine free alternatives. This is a thorny question, but more and more evidence has been gathering to suggest that the answer is YES and that even the best efforts at fluorine free technology falls considerably short of the best fluorotelomer based products on the market, both in terms of fire performance, firefighter safety and environmental impact.

This paper is designed to help unravel some of the confusion that still abounds, clarify some of the more recent findings, and help put minds at rest on this important issue.

Where are we now?

For some time now we have had fluorinated foam manufacturers claiming there is no problem with fluorotelomers and fluorine free products have safety issues for firefighters. At the same time we have also had fluorine free foam manufacturers claiming that fluorotelomers should not be used, that their products perform equally as well or even better than fluorotelomer based products on all types of fires, including polar solvent products which are difficult for any firefighting foam product. Plus there are claims that some fluorine free products have no environmental impacts!

Well clearly somewhere the truth lies lurking! So let's delve into the research to establish an informed base point from which we can make this difficult decision.

As you are probably already aware PFOS (PerFluoroOctanyl Sulphonate) is a fluorochemical ingredient, made by the ElectroChemical Fluorination (ECF) process. It was found in a leading brand of synthetic AFFF and AR-AFFF type foams that were produced before Dec 2002, but fluorinated firefighting foam products were intended to be no longer produced but it is confirmed that Chinese manufacturers have recently entered this market making similar PFOS based AFFF surfactants (Olsen et al, 2008), so the problem may re-emerge and care should be taken when purchasing foams in future that they do not contain these undesirable PFOS based ingredients.

PFOS is a proven Persistent, Bioaccumulative and Toxic chemical and has been banned in the European Union (Europa, 2006). The UK recognises that any foam containing this ingredient should now be disposed of by high temperature incineration (SEPA, 2009).

Using these PFOS products today could risk heavy fines and rectification costs as we saw being imposed after the Dec. 2005 Buncefield fire in the UK, where 22 million litres of fire water run-off

had to be collected, stored and treated by reverse osmosis and activated carbon treatment to remove the PFOS so it did not pollute the environment . Once separated it could be destroyed by high temperature incineration (Environment Agency, 2010).

Do the alternative fluorotelomer based products have similar problems to PFOS?

This has been a difficult question to answer as until recently the conclusions of much research work has not been available, but early indications have always suggested that the two fluorinated chemicals behave very differently.

Chemically the PFOS based AFFF products have both odd and even numbers of carbon atoms in their chains and many have branched isomers , while the fluorotelomer based AFFF equivalent products are all straight chain molecules with no branching and even numbers of carbon atoms, as can be seen from the diagram below. The ECF fluorochemicals break down to PFOS which is highly mobile in the environment . PFOS has been shown to move up the food chain and has been found in fish, penguins and even polar bears where it accumulates in their bodies, is very long lived and is toxic at higher levels. Interestingly limited data gathered by Butt et al (2007) suggests decreasing concentrations of PFOS in Arctic ringed Seals in recent years since ECF production of PFOS based products ceased.

We should clarify that PFOS and its derivatives are not used to make any fluorotelomer based products and are not formed during its manufacture or processing.

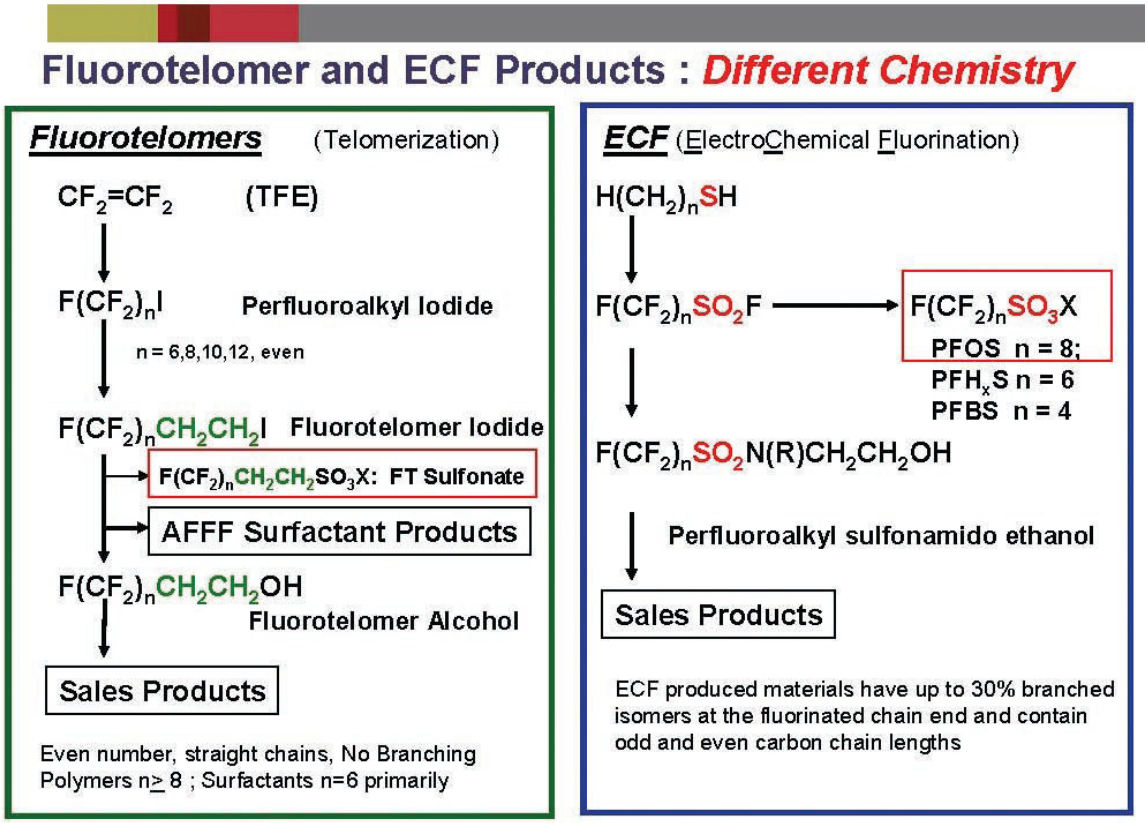

Figure 1: Chemistry comparison between fluorotelomers and Electro Chemical Fluorination (PFOS) based products showing clear differences. (Courtesy Du Pont).

Environmentally these fluorotelomer based AFFF products do not bioaccumulate in animals, do not concentrate up the food chain, are not harmful to organisms and have been shown not to be toxic. Fluorotelomers do not break down to PFOS, they break down to a 6:2 Fluorotelomer sulphonate which although Persistent, it is neither Bioaccumulative nor Toxic (P but not B or T) (Korzeniowski & Cortina, 2008). As the largest fluorotelomer manufacturer Du Pont have proactively conducted extensive environmental fate and behaviour studies with all the results being given to US Environmental Protection Agency (US EPA) as they happen. This has been an on-going program over the last 10 years, but now the results of much of this work is available to us for review.

The results of Du Pont's 10 day oral dosing study on rats have shown that PFOS has very different characteristics in blood samples compared to PFOA, PFHxA (the 6 Carbon chain PerfluoroHexanoic Acid), the 6:2 Fluorotelomer Sulphonate (6:2 FTS) breakdown product of fluorotelomers, and two specific commercial Du Pont fluorotelomer surfactants currently used in some leading manufacturer's foam concentrates (1157 & 1157N). These rats were given a regular high dose of the specific chemical every day for 10 days and then given an 84 day(approx. 3 month) recovery period where they were given no chemicals at all. One would expect virtually all of the product to have either been excreted or broken down over this long recovery period, yet the PFOS result shows high levels have been accumulated in the blood and are still there almost 3 months later, confirming its bioaccumulative or biopersistence status.

The chart also clearly shows that the commercial fluorotelomer surfactants and 6:2 FTS breakdown products of fluorotelomer chemistry do not undergo any bioaccumulative or biopersistence tendancy confirming they are radically different from PFOS and are not bioaccumulative (Korzeniowski & Cortina, 2008).

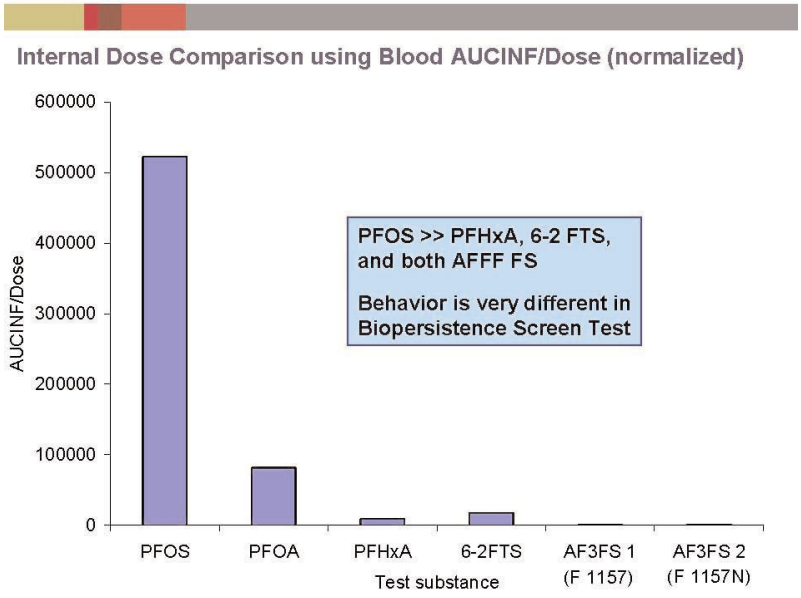

Figure 2: Residual blood level comparison in rats for different fluorochemicals showing PFOS bioaccumulates but Fluorotelomer breakdown products and 2 commercial grade firefighting fluorosurfactant are clearly not bioaccumulative. (Courtesy Du Pont).

Some Fluorotelomer products do contain minute trace amounts of PFOA (PerFluoroOctanoic Acid) as an unwanted by-product from the telomerisation chemical reaction. PFOA was also produced from the ECF process, but PFOA is not an ingredient of fluorotelomer products and there is no known pathway for 6 carbon chain fluorotelomers to break down into 8 carbon chain PFOA (Fire Fighting Foam Coalition, 2005). PFOA is widely used in the production of non-stick pans, electronics and as a processing aid to make high performance fluoropolymer materials, so comes into regular contact with humans from non-firefighting applications. However these biopersistence tests on rat's show that its biopersistence is relatively low (Korzeniowski, 2008).

Many studies have been done on this chemical which although persistent in the environment like all fluorochemicals, it has been shown to be toxic at high levels , but importantly as this Du Pont study shows it is not Bioaccumulative. Hence it is also significantly less problematic than PFOS and Du Pont have confirmed their aim to eliminate the use of PFOA from their products and remove it as a waste product of their production process by 2015 at the latest. The 2009 Annual Progress Report to the US EPA(Environmental Protection Agency) confirms that Du Pont have already reduced the PFOA impurity level in their telomer products by 97% and have reduced their PFOA emissions from production facilities by 99% in US and 96% outside US, so are tracking ahead of their obligations based on 2008 full year data (US EPA, 2009).

Global fluorotelomer production dramatically increased over 5 fold from 1985 to 2000 as it became the major rival to ECF production. However the incidence of PFOS and PFOA in human blood over this period was actually declining. The Centre for disease Control (CDC) section of the National Health And Nutrition Examination Survey (NHANES) in US, found measurable concentrations in all demographic population groups studied. The mean concentrations of PFOA found when measured in 2003-2004 were 25% lower than the 1999-2000 data and 32% lower for PFOS. It was concluded that the cause of these reductions was most likely related to the discontinuation in 2002 of industrial ECF production of PFOS and related compounds (Calafat, 2007). This also confirms that fluorotelomers do not degrade to PFOA, otherwise the human PFOA levels would be rising in proportion to the major increase in fluorotelomer industry production levels. Another study confirmed these results by comparing this CDC NHANES data with American Red Cross data and found very similar results from the American Red Cross Samples of median reductions of 60% for PFOS and 25% for PFOA between 2000-2001 blood serum data and the 2006 blood serum results, as shown in Figure 3 below (Olsen et al, 2008).

As part of their environmental fate and behaviour studies, Korzeniowski 's Du Pont team conducted further research into oral toxicity and developmental toxicity of the specific 1157 fluorotelomer surfactant in rats. Their findings are shown in Table 1 below. This study shows that in a 28 day sub-chronic dose trial where doses from 0mg up to 1,000mg per kilogram of body weight per day were administered to rats, the No Observable Effect Level (NOEL) for both male and females was as high as 200milligrams/kg per day, and even at the highest dosage levels of 1,000mg/kg/day no mortality was seen . Generally the higher the level tolerated the less impact the chemical has on the organism and this confirms that oral toxicity of fluorotelomers in mammals is low.

The developmental toxin test with No Observable Adverse Effect (NOAEL) levels as high as 1,000mg per kg of body weight per day, also clearly shows that it is not a selective developmental toxicant.

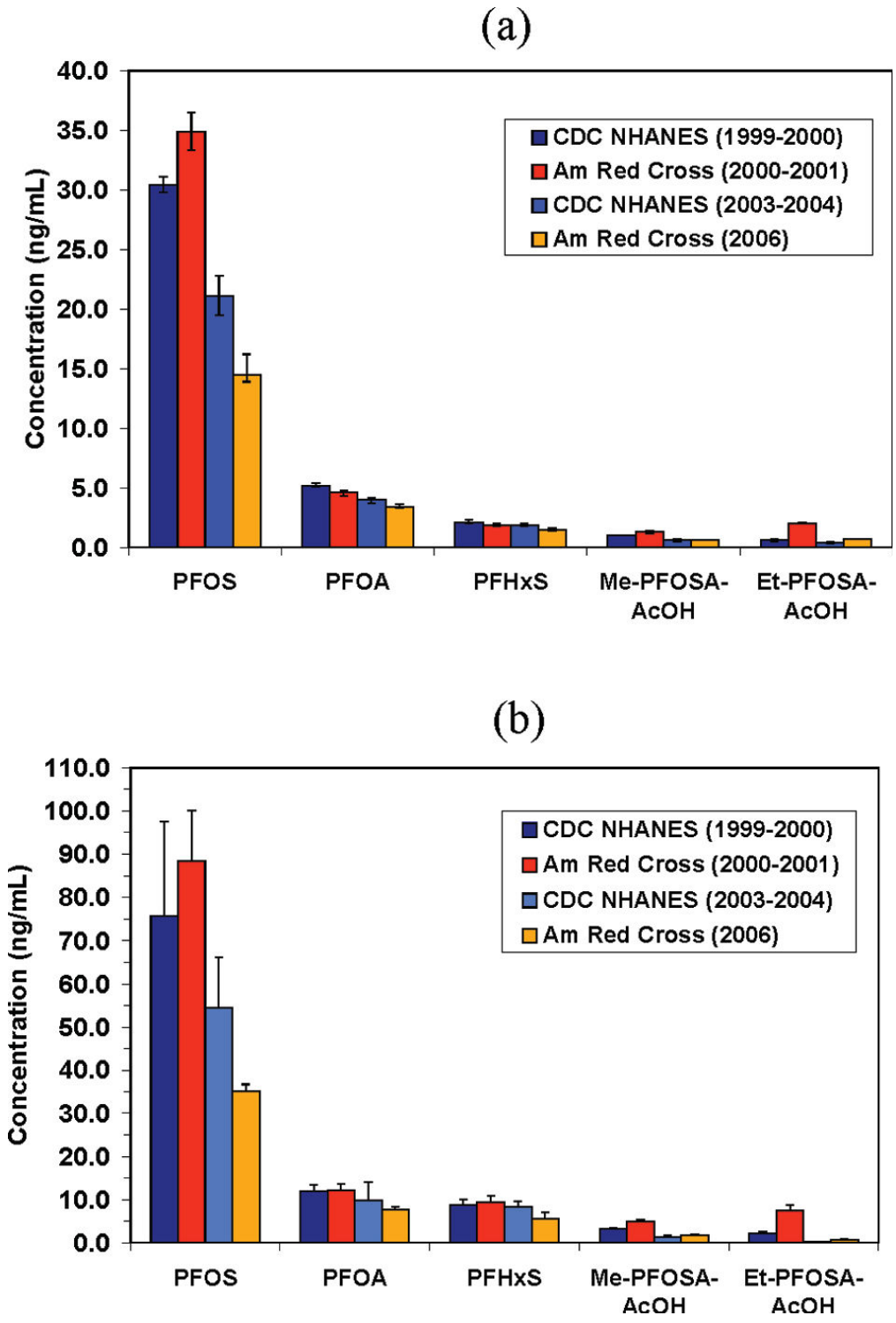

Figure 3: Time trends for PFOS and PFOA concentrations in human blood serum in nanograms/millilitre from the CDC NHANES and American Red Cross study populations. Graph (a) shows the population geometric mean (95% confidence levels), and Graph (b) the geometric mean (CDC NHANES) or estimated 95th percentile tolerance limit (American Red Cross) with their upper 95th percent confidence limits (Courtesy of Olsen et al.).

Similarly in the bioconcentration study conducted under OECD 305 (Organisation for Economic Cooperation and Development) requirements, the BioConcentration Factors (BCF) were very low, again confirming by all assessment criteria that fluorotelomers are not bioaccumulative.

Summary of Toxicity and Bioaccumulation Testing on Fluorotelomer AFFF Surfactant 1157		
TEST DESCRIPTION	**RESULTS**	**COMMENT**
28-day Subchronic Oral Toxicity in Rats	**NOEL for M/F rats is 200 mg/kg/day**	**Doses were 0, 10, 40, 200, and 1000 mg/kg/day. No mortality seen**
Developmental Toxicity	**NOAEL 1000 mg/kg/day**	**Not a selective developmental toxicant**
Bioconcentration in Carp, *Cyprinus carpio,* via OECD 305	**5 ug/L, BCF = < 5.1 50 ug/L, BCF = < 51**	**Whole fish test Very low bioaccumulation potential By all criteria, not bioaccumulative**
ECOTOXICITY: Low-Moderate toxicity in acute fish, invertebrates and bacterial toxicity tests. *CONCLUSION: OF LOW CONCERN*		

Table 1: Summary of oral toxicity, developmental toxicity, bioconcentration and ecotoxicity testing of fluorotelomer AFFF surfactant 1157, as part of the environmental fate and behaviour studies which confirmed it as being a chemical group of low toxicity concern. (courtesy Du Pont).

The Ecotoxicity test showed low to moderate aquatic toxicity to fish, invertebrates and bacteria, but overall the conclusion was that these fluorotelomer products are of low concern (Korzeniowski, 2008) and contrast significantly with historic data for PFOS.

The latest US EPA advice confirms that *"Some telomers are also used as high performance surfactants in products that must flow evenly, such as paints, coatings, and cleaning products, fire-*

fighting foams for use on liquid fuel fires, or the engineering coatings used in semiconductor manufacture. However, consumer products made with fluoropolymers and fluorinated telomers, including Teflon® and other trademark products, are not PFOA. Rather, some of them may contain trace amounts of PFOA and other related perfluorinated chemicals as impurities. The information that EPA has available does not indicate that the routine use of consumer (fluorotelomer) products poses a concern. At present, there are no steps that EPA recommends that consumers take to reduce exposures to PFOA," US EPA 2 (2009). The US EPA also has no preliminary health advisory notices for fluorotelomers, so they are considered safe for continued use. Health advisory notices are a pre-requisite for concerns over any specific chemical listed by US EPA, like PFOS which is listed.

We should also remember that only 5% of the fluorochemicals in the environment come from firefighting chemicals, over 80% are fluoropolymers from consumer products - weather poof jackets to carpets and glossy magazines to non-stick pans (Prevedouros et al. 2006). They should all be used responsibly, contained when used, collected after use, and disposed of safely - sound advice applicable for virtually all chemicals.

Why are these fluorotelomers so important for firefighting?

Fluorotelomers play a vital role in modern firefighting, by helping firefighters achieve their objectives in a safe and rapid manner. They provide fast control and extinction under a diverse range of flammable liquid applications. They help minimise spread of the fire, prevent re-ignition and reduce the amount of airborn smoke pollution. Foams containing these important fluorotelomer chemicals also protect casualties and firefighter lives, by reducing the risk of flare up , flash backs and preventing rapid escalation. Additionally they avoid the risk of boil-overs and escalation that can occur from "let it burn" policies, and ensure that minimal foam and water resources are used in any given incident. Significant asset protection is also provided by their use, reducing damage to property and investments, minimising business interruption and financial losses so the overall disruption of the fire incident is minimised.

A recent paper from the University of Newcastle in Australia confirmed that even the best available fluorine free foams would need replenishment three times as often as good quality AFFFs to provide the same level of fire protection. (Schaefer et al, 2007). Interestingly they also found most Fluorine free products had almost no sealing ability on AVGAS vapours.

Are Fluorine Free Foams really environmentally friendly?

Fluorine free foams are often championed as "environmentally friendly" alternatives to fluorotelomer based foams. Others will claim they are "drop- in replacements" but their environmental profile related to biodegradability, acute toxicity, chemical oxygen demand and biological oxygen demand is in many cases significantly less environmentally responsible than fluorinated foams. Problem is that when the fluorochemicals are removed, there is no direct replacement because they are a unique group of chemicals. Some substitute ingredient is still needed to maintain a level of fire performance, so Fluorine Free Foams rely on additional synthetic detergent ingredients being added, which can lead to sudden flashbacks and dangerous situations

for operational firefighters. That's why achieving high performance in a fluorine free product is so difficult for everyone. The more volatile the fuel, like gasoline, the more fuel is likely to be picked up in the foam blanket, waiting like a time bomb to ignite. It is when the blanket begins to drain that the problems start, as fuel vapour as well as air is released above the foam blanket leading to unpredictable behaviour from minor flaring to major flashovers (Willson, 2007). The more detergent in the foam, the more fuel is likely to be picked up, and the more forcefully it is applied to the fuel the more fuel can be picked up , so it can suddenly burst into flames and the whole blanket can breakdown within 60 seconds , which the author has witnessed on numerous occasions.

The problems don't stop there. Such detergent containing foams also emulsify with all oil based fuels (the more detergent the more emulsification) and carry them past waste water separators, into the aquatic environment. This gives rise to much higher oxygen demands, toxicity to aquatic organisms living there and potentially major pollution incidents. Extreme care need s to be taken, particularly when handling these Fluorine Free products, as even small spillages can have significant consequences to any water source.

So although there is a perceived benefit by being Fluorine Free, there are several significant disadvantages in terms of environmental toxicity, emulsification with hydrocarbon fuels and sudden flashbacks, putting the safety of firefighters at considerable extra and unnecessary risk.

Some foam ingredients are safer for use than others?

The fluorochemical content in foams comprises only a small part of the ingredients in the foam concentrate, typically accounting for around 1-10% depending on specific product and type. Another 10-20% being the foam booster - glycol ethers in detergent AR-AFFFs or the more benign hexylene glycol boosters (5-10%) in the protein based AR-FFFP products. Water soluble polymers (typically below 5%), hydrocarbon surfactants (less than 10%) and water make up the balance in detergent based AR-AFFFs, while the protein based AR-FFFPs also contain up to 30% hydrolised protein, mineral salts (1-10%), and less than 5% preservative to provide long storage life.

Looking at the Material Safety Data Sheets (MSDS) for ingredients in the major leading international brand fluorotelomer fire fighting foam products shows they do not represent a hazard for firefighters handling the product. Normal precautionary protective clothing of goggles and rubber gloves are recommended, and are normally diluted by a factor of almost 100 for use strength when applied to a fire. FluoroProtein foams continue to provide the most efficient use of fluorotelomers with concentrate levels typically 10 times less than some leading AR type products (MSDS sheets, courtesy of Angus fire).

Some Fluorine Free Foam products also have additional protective recommendations to firefighters on their MSDS. A leading Fluorine free product recommends *"when handling the product wear a gas mask with filter A if concentrations in air rise above exposure limits of 10 parts per million(ppm)",* which is a very low level. Handling the product is also *"recommended under local exhaust/ventilation systems"* to try and ensure exposure levels do not build up above recommended levels around the container while decanting (Solberg RF3x6 MSDS Sheet, 2007). Additional hazards raised on this

MSDS sheet are that it is categorised as Hazard category R51/53 defined as *"toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment"*. In the ecotoxicity section for effects on waste water purification it states that the product is *"harmless to activated sludge at sufficient dilution"* – aren't they all! But there is no indication what this dilution factor should be, so like most strong detergents it is likely to disrupt water treatment processes and kill the bacteria that they rely on to operate correctly, unless high dilution factors are implemented.

People ask Why are there such huge variations between products?. The answer lies in synthetic detergent being the most toxic ingredient used in foams and consequently many of these Fluorine Free Foams are highly toxic to aquatic organisms in the environment as they have elevated detergent levels. If they creep into water sources, rivers or lakes they can kill fish and other organisms. In tests on Rainbow Trout it takes only around 65-70 mg/L (parts per million) of a typical Fluorine Free Foam in water to kill 50% of the fish swimming in it, whereas a high performance fluorinated foam would require around 2000mg/L to kill these fish and a typical AR-AFFF would require 3,500mg/L to kill those same fish . This shows that it would require an amazing 53 times more fluorinated AR-AFFF to be spilt in a river, to affect the fish as badly as the far smaller amount of Fluorine Free Foam! When large quantities of foam can be quickly used in response to large incidents, this is especially relevant for firefighters to consider in their risk assessments.

Fluorine Free foams do have an important role to play in training and vehicle calibration where they can mimic the induction performance of fluorinated foams, and can be used in non-emergency training situations where controls can be put in place to ensure the safety of firefighters.

Given what we know about persistence, Fluorochemicals were always considered indestructible, but a study published for the 4th Fire fighting Foam Conference at the UK's Reebok Stadium in July 2009 confirmed that studies involving a 6:2 FTS had degraded by 10% to a C5 perfuorinated species in nature (Korzeniowski, 2009). Coupled with the release of DuPont's shorter chain Capstone fluorotelomers which contain 6 or fewer perfluorinated carbons in the chain they are able to retain high performance while reducing potential environmental impacts (Reicher, 2008). Maybe fluorotelomers are not as bad as many perceive – the evidence has been building for some time and is virtually now complete to confirm this view.

Conclusions

1. ***Fluorotelomers are neither toxic, bioaccumulative nor biopersistent*.** PFOS is proven Persistent Bioaccumulative and Toxic. Rat and fish studies conducted on 6:2 FTS breakdown products and Surfactant 1157 confirmed that fluorotelomers are not bioaccumulative nor biopersistent. The environmental fate and behaviour studies from rats have shown no oral toxicity to fluorotelomers and they are not a developmental toxin. Ecotoxicity testing concluded that fluorotelomers are of low ecotoxicity concern.

2. ***Fluorotelomers are safe for continued use*.** The human blood studies show declining PFOA levels at a time when fluorotelomer production increased 5 fold, proving beyond doubt that

fluorotelomers do not degrade to PFOA. PFOA impurity levels have already been reduced 97% by Du Pont in fluorotelomer products and manufacturing emissions have been reduced by at least 96%, ahead of their expectations and confirmed by the US EPA. The US EPA confirms that the routine use of these fluorotelomer products does not pose any concern, they are safe for continued use. Other foam ingredients in these fluorinated foam concentrates are of low concern for firefighters as shown in the product's MSDS. We tend to forget they are also diluted almost 100 times at normal firefighter use strength.

3. ***Fluorotelomers provide unique benefits to firefighters.*** Fluorotelomers play a vital role in providing fast control and extinction of all flammable liquid fires under a diverse range of situations, minimising the spread of fire, resisting re-ignition, reducing smoke pollution, protecting casualties and keeping firefighters safe from dangerous flare-ups, flashovers and preventing rapid escalation, while minimising the use of foam and water resources.

4. ***Fluorine free foams are highly toxic, emulsify with hydrocarbons and breakdown suddenly.*** Championed by some as "environmentally friendly" fluorine free foams have been shown to be highly toxic to most aquatic organisms, plus bacteria used in waste water treatment facilities. They also emulsify with hydrocarbon fuels, can carry them past fuel separators into the environment causing potentially severe pollution incidents, and can breakdown suddenly under fire conditions, so they need to be handled with extreme care. It would require around 50 times more AR-AFFF to be spilt in a river to kill fish, than most Fluorine Free Foams and research shows it would need replenishment three times as often as good quality AFFFs to provide similar fire protection. When large quantities of foam are being used in major incidents this is a significant risk assessment consideration.

5. ***Fluorine free foams need to be handled with extreme care.*** Synthetic detergent is the most toxic ingredient in most fire fighting foams and increased levels used in fluorine free products accentuate these problems. Gas masks are recommended when handling some Fluorine Free Foam products as safe exposure limits are apparently as low as 10 parts per million in air! Fluorine free foams do have an important role to play in vehicle calibration and firefighter training, where controls can be put in place to contain firewater run-off and ensure adequate firefighter safety.

6. ***Benefits of latest fluorotelomer products****.* Recent research has shown that the fluorotelomer breakdown product 6:2 FTS has naturally degraded by 10% to a C5 perfluorinated species. The latest shorter chain (6 and less) Capstone fluorotelomer products retain high performance while further reducing their potential environmental impacts.

Time to make up your own mind...

Each Fire Authority, industrial organisation and foam user must make up their own minds, based on their experiences, research, testing, hazards and environmentally sensitive areas to determine which

products give them the best performance, flexibility, all round capability and safety for their firefighters and operational fire duties.

Most fire authorities and industries involved with flammable liquids have conducted their own evaluations and tests on both types of these foams. Many I have talked to have retained their commitment to fluorotelomer based foams, particularly since the science now confirms they are safe for continued use, still provide the best performance, most effective, safe and reliable method of fighting fires, and importantly remains the method for using least foam and water resources for a given sized incident. It was interesting that the mood at the Reebok conference in UK last July was one of realisation that fluorine free products did have serious limitations, and modern fluorotelomer based products provided the most secure, effective and safe products for firefighters to use into the foreseeable future.

Ultimately, we hope that fluorine free products -without the current drawbacks -will be developed, but they will probably utilise new ingredients not used in foam before, to achieve these challenging objectives. We have gone as far as we can with existing fluorine free technology. It requires a quantum shift to gain the performance we are seeking without the use of fluorotelomers, but that still seems a long way off.

Mike Willson ©March 2010

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