ANGUS FIRE

# FOAM LINK

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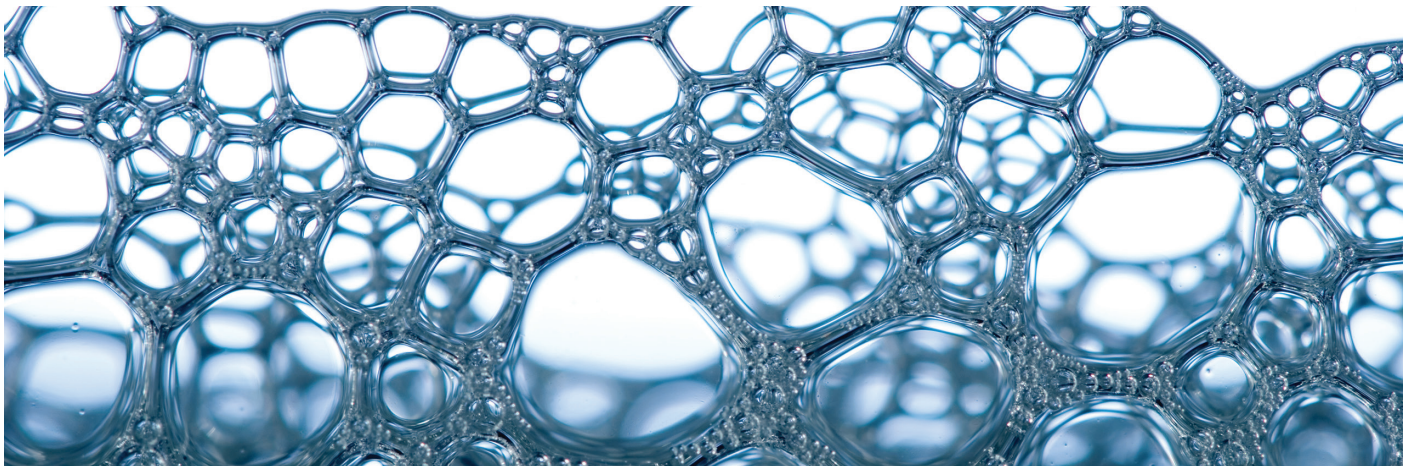

# Fire Fighting Foam – The Essential Chemistry

by Nigel Joslin

## Reports of my death have been greatly exaggerated[1]

That may not have been your first reaction on hearing about the commotion surrounding the release of the Madrid Statement as featured on the HemmingFire IFJ website. According to the shocking headlines it seems that the worldwide scientific community has finally woken up to the harm caused by perfluorinated chemicals being used in commercial products and more importantly in AFFFs.

Yes the game is up and even the much heralded C6 fluorochemistry is implicated.

But before we write the obituary for AFFFs and their fluorinated partners in crime, let's look a bit more closely into the background of the Madrid Statement and also why, despite the continued bad press, fluorochemicals refuse to go away. (It's all down to their persistence you know).

## The real Madrid Statement

At first sight the Madrid Statement looks both impressive and disturbing. A group of scientists, many from the world of academia, has lent its support to a statement calling for research, monitoring and even restricting the use of poly- and perfluorinated alkyl substances (PFAS). As part of a two pronged approach, this should also include the provision of non-fluorinated alternatives and the development of novel replacement chemistries.

By its nature the Madrid Statement takes a broad overview of the environmental impact of all PFAS irrespective of their type and application, which means that those included in fire fighting foams are tarred with the same brush. However this approach is somewhat naïve as it ignores the body of evidence already accumulated regarding those fluorochemicals used in formulating foams. Because of the potential for release into the aquatic environment, the likely degradation products of AFFFs and their fates have already been extensively studied by the fluorochemical manufacturers. The consensus is that the main degradation product is the fluorotelomer sulphonate (6:2 FtS) and despite scare stories to the contrary it shares few similarities with perfluorooctane sulphonate (PFOS). The presence of 6:2 FtS in the environment was first disclosed in a seminal paper by Dr. Jennifer Field[2] (a name that will reappear later in this article) and its environmental profile is well documented[3].

It would be disparaging to dismiss the Madrid statement as a knee jerk reaction by a group of well-meaning eco activists. After all, the problem of the persistence of PFAS is well known and generally accepted, and no one could argue against improvements to their chemistry which do not compromise on performance.

Yet both the current situation and the medium term suggest that there will be no restriction on the emergency use of fire fighting foams containing organofluorine.

Similarly it should be stressed that the Madrid Statement is simply the view of a lobby group; no more, no less. Significantly it does not contain signatories from the chemical industry, the fire safety sector or government research groups. Nor does it enjoy the support of individual nations or influential collectives such as the World Health Organisation (WHO) or the Stockholm Convention on persistent organic pollutants (POPs).
Rather than attracting backing from a truly wide ranging support base, it relies heavily on individuals dedicated to working on environmental and sustainability issues.
In other words, only those with a somewhat vested interest in the subject and consequently representing a selective part of the scientific community.
Furthermore it is the view of a group wholly ignorant of the challenges posed by large fires involving flammable liquids, with all the attendant dangers that these pose to responders.
Surely it cannot be the intention of the signatories to deprive fire fighters of their best tools for the job?

Indeed, closer inspection of the Madrid Statement reveals that this is not the case. It acknowledges that there will be a requirement for *essential* uses of PFAS and I think that we can all agree that fire fighting would fit in that category.
On reviewing the Green Science Policy Institute website which both originated and hosts the Madrid Statement, it reveals an informative fact sheet on PFAS as written by Dr. Jennifer Field, the aforementioned authority on the environmental fate of AFFFs. In it she acknowledges that there are situations *where they may provide an important safety factor,* and only questions their use for mundane applications.

So to recap; we should not be overawed by the excitement which has accompanied the Madrid statement and view it as a 'game changer'. It is effectively just a petition questioning the non-essential use of PFAS, as signed by an interested lobby group, and no different from any other protest campaign.

## The fluorine free foam fallacy (F4)

It is pertinent at this point to remind ourselves why PFAS are critical to the high performance of modern day foams.
To be truly effective, foams need to have the following characteristics:

- Oil repellency
- Tolerance to contamination
- Vapour sealing ability

Without any of these they are inherently flawed and cannot be expected to achieve the level of performance necessary for the rapid control and extinguishment of flammable liquids.
To understand what makes these characteristics so important, we need to look at each in greater detail.

**Oil repellency:** By this we mean the ability of individual foam bubbles to shake off any oil droplets that they may come into contact with, in a similar way to which carpets are treated to prevent them staining.
Both rely on the inclusion of PFAS since it is only the unique properties of the fluorine atom which can impart oil repellency.

In the case of fire fighting foams, the example par excellence can be seen in their use for sub-surface injection. Here the foam is deliberately introduced into the base of a tank of hydrocarbon oil and is allowed to rise to the surface to establish a blanket.
This is the ultimate test of oil repellency; which is only made possible by the inclusion of PFAS, and not surprisingly, fluorine free foams (F3) are unable to work in this manner because they do not possess this property.

**Tolerance to contamination:** When foam is applied forcefully by monitors or cannons, it is inevitable that despite the presence of oil repellent fluorochemicals, there will still be some contamination due to the turbulent mixing between the oil and aqueous phases.
For fluorine free foams this effect will be even more pronounced[4].

How this contamination affects the subsequent stability of the foam blanket depends on the fuel tolerance exhibited, which itself is a direct consequence of the various tensions at the oil/water/air interfaces.
Oil droplets can de-stabilise foams by entering the blanket and forming bridges between adjoining bubbles or by spreading over bubbles, causing localized thinning and leading to eventual rupture.
The propensity of oil to do this can be calculated from the Entering Coefficient (Eow) and the Spreading Coefficient (Sow) respectively. Furthermore it only happens when Eow or Sow are positive[5,6].
Both coefficients are mainly influenced by the value of the foam surface tension, which itself is dependent on whether the foam is formulated with PFAS. AFFFs have such low values of surface tension that Eow and Sow are always negative, meaning that oil droplets will neither enter in nor spread over the foam blanket, so that it remains stable even in the presence of hot fuel.
Fluorine free foams however have relatively high values of surface tension to the extent that Eow and Sow can be positive, thereby leading to premature collapse of the foam blanket due to the effects of oil contamination.

**Vapour sealing ability:** One of the main mechanisms whereby foam blankets extinguish fires is by forming a barrier which prevents vapours coming into contact with an ignition source, so sustaining the flames.

The effectiveness of this vapour barrier is governed by its permeability which in turn is influenced by a number of factors such as vapour pressure and foam depth, but also by the surfactants that are used to stabilize the bubbles.

Vapours cross through individual bubbles by a process known as diffusion and it is the chemical nature of the bubble walls which largely determine how quickly this happens.
Research has shown that bubbles made from PFAS act as a much more effective barrier to the transit of fuel vapour than do those only containing hydrocarbon surfactants as with fluorine free foams[7].

The positive benefits of PFAS on vapour sealing were demonstrated in a series of tests carried out by the University of Newcastle, Australia[8]. They conclusively showed that AFFF had a vapour sealing lifetime of three times that of fluorine free foam for a given application

Large scale flammable liquid fires are difficult enough to tackle at the best of times, and any fire fighter must be confident that his foam has the right attributes to do the job, whilst still maintaining his personal safety.
PFAS were introduced into fire fighting foams for good reasons, not least to impart oil repellency, fuel tolerance and long term vapour suppression. Omitting them as in fluorine free foams makes them less effective, actually sets back foam development years and increases the exposure of fire fighters.

## What's in a number?

No one pretends that fluorinated chemicals are perfect, and the history of PFOS and perfluorooctanoic acid (PFOA) reminds us that we need to remain vigilant to prevent Persistent, Bioaccumulative and Toxic (PBT) substances being released to the environment.

To its credit the chemical industry has made great strides in reducing the overall environmental impact of PFAS, not least by moving from what is known as C8 to C6 chemistry.
In simple terms the number denotes how many carbon atoms are populated with fluorine atoms. So a C8 molecule has eight, but a C6 molecule only has six.

Why have the fluorosurfactant manufacturers done this? Well the simple answer is that they worked in cooperation with the EPA to reduce the environmental impact of their products. .
What it means is that the new C6 chemistry will not contain or produce PFOA. A further benefit is that PFAS made from C6 will be less toxic and bioaccumulative than their equivalent C8 homologues. This has been confirmed by both the manufacturers[9] and independent researchers[10].

All of these improvements would be futile however if they had been at the cost of compromising fire performance. Fortunately this is not the case and the latest C6 fire fighting foams being rolled out, have equivalent, if not better ratings than the C8 products they are replacing.

Furthermore this has been achieved with no increase in fluorine content and in some cases, even a reduction.

## Burning issues

If you have read this far then you are nearing the end of yet another article in the seemingly interminable debate on fluorine versus no fluorine. Unfortunately there seems to be no end in sight, since those of us on either side are well entrenched in our respective positions. Ultimately it seems to be a question over conflicting priorities between the environment and fire safety, and which is deemed to be more important.

If the thinking is that the environment should come first, then the argument appears to be solely about the long term persistence of PFAS and whether or not they could be detrimental. It is one of those questions that we might never be able to answer satisfactorily, because it relies on us predicting the future. Furthermore it ignores any short term effects such as toxicity and presents us with a much skewed view of the environmental profile of fire fighting foams. After all, irrespective of whether they contain PFAS or not, all foams pollute[11].

Conversely if the priority remains one of fire safety, including that of responders, then surely only the best should be good enough. Why would you ever choose a product where all the vital components have been removed?
Certainly the oil and petrochemical sector has not been convinced that swapping to F3 will not compromise its capability to deal safely and effectively with large flammable liquid fires. Even for those users who have already embraced F3, some are now beginning to regret their decision.

What sparked this latest round of debate was the release of a petition into the public domain by a lobby group. With all the excitement it generated, let's not forget that it remains the opinion of some people with a scientific background, but who have no knowledge or experience of the complexities of fire fighting.
As with any group they are entitled to hold an opinion, but we should not allow ourselves to be unduly swayed by what is after all, one voice in a global scientific and technical community.

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*Nigel Joslin has worked for Angus Fire as a development chemist, plant manager, R&D manager and most recently as technical specialist. With many years experience in the formulation and application of fire fighting foams, he is currently chairman of the FIA working group.*

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