Am I alone in thinking?

It is now 10 years or more since fluorine free foams (F3), first became available. Since those early days a greater number of products for more class 'B' applications have been developed by many manufacturers. Simultaneously, the level and variety of their respective approvals have gradually increased to the point where, on paper at least, they look every bit the equal of their fluorine containing counterparts.

Introduction

If this is the case then it represents a radical change in the development of fire fighting foams, because the fluorinated chemicals that go into traditional foams like AFFFs, have for many years been the building blocks of all operational products used on flammable liquid risks.

> *"Until the 1960s there were no fluorine containing foams and the only ones available were fluorine free types, except they weren't called that then."*

Coupled with the expense of fluorinated chemicals and ongoing concerns about their persistence, F3 foams would appear to offer an economic, technical and environmental advantage over anything that fluorine can do.

So it looks as if this is a situation where there are only winners. The manufacturer can put his specialist and expensive fluorochemicals back on the shelf, whilst the end user gets all the benefits of fully approved products with no apparent loss in fire performance. And for mankind in general, any potential threat to the aquatic environment is averted.

But (and unfortunately there does seem to be a 'but'), the more I look into this, the more puzzled I am about certain aspects of this move from fluorine containing foams to F3; particularly in high risk sectors such as aviation.

Am I alone in thinking that we know precious little about the technical and environmental background to F3 foams, and what we do know should give us cause to re-consider?

On the one hand there is the complete lack of any scientific hypothesis offered as to the mechanism by which F3 foams operate and the critical components formulated within, that give them their efficacy.

On the other, there is the wide spread assumption by some users, manufacturers and even regulators that any fluorine is bad, whereas no fluorine is good, irrespective of the chemical composition of the foam types being compared.

It seems to me that these issues need closer attention, since without understanding the scientific and environmental detail, we risk making important procurement decisions on information that is incomplete or even ill informed.

And it should be science and hard data that guides our judgement, rather than unquantifiable predictions of environmental catastrophe and pseudo-scientific explanations with a suitable marketing spin.

So I offer for consideration, the following issues which I find troubling……………

F3 foams seem to defy rational explanation

Firstly my apologies for having to invoke some chemistry, but please bear with me.

Most fire professionals are familiar with the concept of aqueous film formation, whereby manipulation of the various tensions at the oil/water/air interface allows for the establishment of a thin aqueous film on top of the burning fuel.

Prediction of this film forming effect is given by a positive value of the water-on -oil spreading coefficient S_{wo} and is the basis for the rapid knock down and extinguishment achievable by AFFF foams on shallow pool fires.

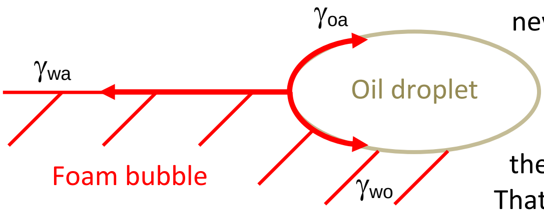
Less well known however is the reverse of this effect, known as the oil-on -water spreading coefficient S_{wo} which has an equal role to play in predicting the behaviour of aerated foam, when applied to a burning hydrocarbon.

So if we consider foam landing on a pool of aviation fuel from a vehicle monitor, then the impact velocity will be high and it will promote mixing of the foam with the fuel.

When looked at on the individual bubble scale we can appreciate what effect the surface chemistry has on the outcome.

Whether or not the oil droplet spreads over the bubble surface is given by:

$$S_{ow} = \gamma_{wa} - \gamma_{oa} - \gamma_{wo}$$



where;

γ_{wa} is the foam/air tension

γ_{oa} is the oil/air tension

γ_{wo} is the foam/oil tension

If $S_{ow} > 0$, then the oil droplet will spontaneously spread over the bubble, leading to thinning of the walls and eventual rupture. This will happen even in the absence of flames and is more pronounced as the fuel temperature increases.

By putting in some figures for AFFF and F3 foams we can see how they both react to forceful application onto aviation kerosene.

For an AFFF, γ_{wa} is typically 18mN/m, γ_{wo} is typically 2 mN/m and γ_{oa} for Jet A1 is 23.5mN/m.[Ref 1]

Doing the maths we get $S_{ow} = {}^{-}7.5$.

So Jet A1 does not spontaneously spread on the AFFF surface, which of course is no surprise, since the opposite is actually the case. Namely that AFFF solutions spontaneously spread on Jet A1.

A similar exercise for F3 foam means that we have a value of 28 mN/m typically for γ_{wa}. Values for γ_{wo} and γ_{oa} are the same as before. Now when we calculate S_{ow} we get a result of 2.5, predicting that this time the Jet A1 will spread.

This is significant because it means that F3 foams are fundamentally unstable with regard to the effects of oil contamination[Ref 2,3].

Because they do not contain the fluorochemicals which alone can lower the surface tension sufficiently to render S_{ow} negative, they are open to attack from the spreading effects of oil, leading to foam collapse and loss of blanket integrity.

So the underlying surface chemistry leads us to conclude that the current generation of F3 foams can never be sufficiently stable on hydrocarbon oils to make them as effective as the fluorine containing foams they are meant to replace.

That's not to say that in the future it won't be possible, but at the moment the technology has not been developed that can accomplish it.

What has fluorine ever done for us?

I can well appreciate that for some people the surface chemistry argument expounded previously is either unproven or just plain irrelevant. They have seen the fire test evidence or certificate of approval with their own eyes and that is enough confirmation they need.

So perhaps this exercise in logic that follows will give food for thought?

Fire fighters tackle a fire using foam

Until the 1960s there were no fluorine containing foams and the only ones available were F3 types, except they weren't called that then.

Then the 3M Company introduced the first Lightwater™ products and a host of others soon followed. These new fluorinated foams were demonstrably superior and allowed for lower critical application rates with no compromise in performance.

Subsequently a new generation of F3 products have been marketed which supposedly match the performance of those fluorinated foams which themselves were of proven superiority to the original F3 foams.

However the materials used to formulate the latest F3 foams are no different to those that were available to chemists when AFFFs first arrived. Seeing as the first AFFFs were very expensive compared to foams already in use, it should have been possible to match their performance there and then without recourse to using fluorine. The economic advantage of not going down the fluorine route would have been a big incentive to remaining fluorine free. Yet the performance benefits of AFFFs were overwhelming, even given the extra cost, because of the unique properties afforded by the addition of fluorinated surfactants.

> *"It would be naïve to believe that any fire fighting foam is environmentally benign, but there has been a perception that somehow fluorine free foams are more acceptable for use"*

But now we seem to have concluded that fluorine is no longer needed to achieve best performance even though the new generation of F3 foams is fundamentally no different from the original ones.

In short: originally we didn't have fluorine, then we decided we couldn't do without fluorine and now we have decided that we don't really need fluorine after all. How can this possibly be when the F3 alternatives haven't really changed in the intervening period?

Where is the peer review?

When it comes to tackling the puzzling inconsistencies surrounding the fire performance of F3 foams, we should also consider the topic of peer review.

Peer review in scientific terms is all about the scientific community being able to replicate and confirm independently what is being claimed by one of their number. Only then does a new theorem gain credibility and become generally accepted.

Similarly we can apply the same principle to claims made by proponents of F3 foams. It is all very well having a piece of paper stating that a product is approved to a certain standard, but can that approval be validated by others within the industry?

If it cannot, then there have to be concerns over the test conditions and parameters adopted for the original type approval, the combination of which for whatever reason, appears not to be readily reproducible.

From personal experience of most of the F3 foams available on the market today, it seems that none can be fully substantiated in terms of the performance claims made. Not surprising you are probably thinking, seeing as I have a vested interest in questioning their merits. And it is a fair point, in that my opinion as a spokesperson on behalf of an AFFF supplier can hardly be taken as truly objective.

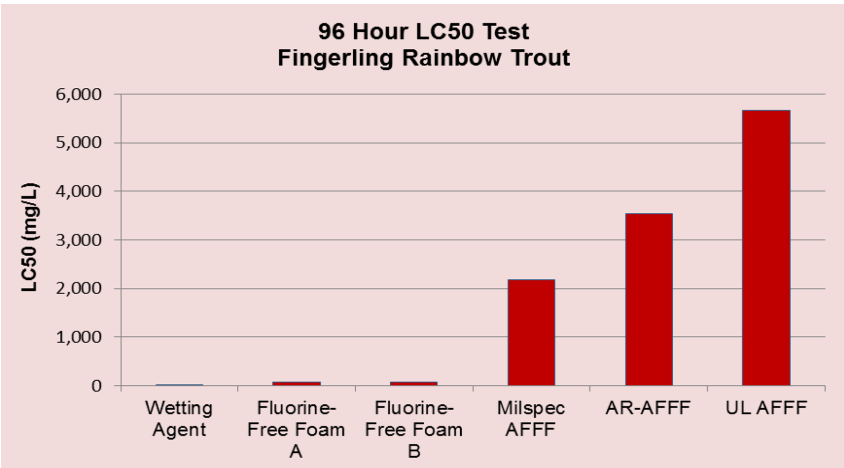
So in the interests of greater independence, an accredited European test house was contracted by Angus Fire to carry out a series of fire tests on F3 products to a recognized international protocol. They also concluded that none of the F3 foams tested were able to perform according to the claims made by the manufacturer.[Ref 4.]

This problem of independently replicating claims made for F3 foams is even more widespread and has been confirmed by other parties. In 2013 a series of tests were sponsored by Dynax Corporation[Ref 5] and carried out in Denmark under the auspices of Resource Protection International. The EN1568 protocol was followed and again the results suggested that the approvals claimed for the F3 products were largely not sustainable.

In hindsight this is to be expected, as we have already seen that the surface chemistry predicts an absence of oil repellency in F3 products. This in turn will undermine the integrity of the foam blanket, impairing its ability to provide an effective vapour seal and leading to premature collapse. Little wonder that they struggle to perform as effectively as fluorinated foams, around which these test protocols were originally devised.

There's something fishy going on

Moving away from the uncertainty surrounding the fire performance of F3 foams, it is time to focus instead on the environmental claims. Certainly there can be n o doubt that being devoid of organofluorine means that these products can theoretically



Test results; the bigger the bar, the less toxic the chemical [Ref 6] biodegrade completely in the aquatic environment without leaving any organic residues.

By contrast, there is a small but significant part of fluorinated foams that is persistent and which could potentially have a half-life of tens and even hundreds of years.

The pertinent question is whether this really matters, and it is one for which there isn't a definitive answer yet. It should serve to promote more study and research into what the long term effects are likely to be, but the general consensus coming from regulatory bodies within the EU and also the US EPA, is that fluorine containing foams can continue to be used responsibly as emergency situations dictate.

It would be naïve to believe that any fire fighting foam is environmentally benign, but there has been a perception that somehow F3 foams are more acceptable for use because they do not contain fluorine, which as we all know is bad. Except we don't know that for certain yet, apart from a couple of specific chemicals. Namely PFOS and PFOA.

Environmental effects can result from other unwelcome attributes of foam, such as toxicity and bioaccumulation, so it is taking a rather selective attitude to focus purely on the persistence of fluorinated foams to the exclusion of all else.

For example if we were to look at the comparative toxicity of F3 foams with AFFFs, then it might lead us to a different conclusion as to which is the environmental villain.

A study on the aquatoxicity of foam compounds compared three AFFFs with two F3 foams and a wetting agent[Ref 6]. The results demonstrated clearly that the AFFFs were less toxic to fish by a significant margin.

Similarly, work done by CRC Australia and presented at the 4th Reebok Foam Conference in 2009[Ref 7] confirmed that the toxicity of F3 foam to aquatic organisms and plants far exceeded that of both telomer based AFFF and even one containing PFOS.

PFOS, the chemical whose name must not be mentioned, and yet the industry seems comfortable in promoting the use of F3 foams even though they could be more toxic than a banned product.

Truly we appear to have got ourselves into the bizarre situation where persistence trumps everything else in the environment stakes and other potentially damaging traits are all but ignored.

Conclusion

There are sufficient unanswered questions surrounding the performance and environmental credentials of F3 foams to make us stop and think.

The underlying chemistry predicts that they are much less effective than their fluorinated counterparts.

History teaches that the advent of fluorine introduced into foams, produced a marked improvement in performance and commensurate reduction in application rates. Somehow however, these favourable, lower rates can now be realized by taking out the very chemicals that made them possible in the first place.

Meanwhile beyond the approvals claimed for F3 products, it is becoming increasingly difficult to validate their performance and instead it is apparent that independent results are actually confirming what the chemistry leads us to believe. Which is, that these products are fundamentally flawed.

Even their environmental credentials give cause for concern. Fluorine free and biodegradable they may be, but at what cost for aquatic and plant life?

We should all be in favour of improvements within the fire industry that are measurable and sustainable, and naturally the case for more environmentally benign foams is unarguable.

What concerns me is the growing body of evidence suggesting that the current generation of F3 foams is not the panacea we would all wish for.

Unless I am otherwise mistaken?

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