

Siloxane-Based AFFF: Testing of Experimental Foam Concentrates

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Introduction

Aqueous film forming foams (AFFF) are the most effective fire extinguishing agents for pool fires but classic AFFF possess a severe disadvantage. They show a negative environmental behavior because of the imperatively contained polyfluorinated surfactants (PFS). PFS build a subgroup of the polyfluorinated compounds (PFC). PFC are generally known for their chemical stability and their high persistence in nature. For the subgroup of PFS the situation is more serious than for the PFC. Additionally to their persistence some of the PFS are proven as bioaccumulative and toxic.¹ For that reason the use of PFS is increasingly restricted by law. Examples for this ongoing restriction process are in the European Union and the United States.^{2,3} On account of the proven persistence and the possible bioaccumulation and toxicity the Drinking Water Commission of the German Federal Ministry of Health defined very low acceptable limits for PFS in water.⁴ The concentration of PFS in AFFF solution is approximately five orders of magnitude higher than the acceptable limit for drinking water. This low acceptable concentration of PFS in drinking water leads to the problem that the use of AFFF can easily affect the drinking water supply of a nearby city. Examples for the contamination of drinking water sources with PFS are known worldwide.^{5,6,7} Because of this situation the use of AFFF is increasingly critically seen by the environmental authorities. A ban of PFS, which would lead to an indirect ban of AFFF, seems possible for the future. In search of environmentally acceptable alternatives, the Bundeswehr Research Institute for Protective Technologies and NBC-Protection is working on a PFC-free siloxane-based AFFF for use on militarily relevant fuels, i.e. the NATO standard fuel F-34 or Diesel.^{8,9,10}

Background

Table 1: Surface tensions of important fuels.

	Fuel	SFT_F (24 °C)	Sample Origin
1.	FAME (Biodiesel)	31.5 mN/m	BP Refinery Emsland, Germany
2.	Diesel	28.3 mN/m	BP Refinery Emsland, Germany
3.	Jet fuel	26.7 mN/m	BP Refinery Emsland, Germany
4.	F-34	25.8 mN/m	Bundeswehr (NATO Standard Fuel)
6.	Gasoline	20.7 mN/m	BP Refinery Emsland, Germany

PFS are added to AFFF to establish a surface tension of the foam solution (SFT_A) which is significantly lower than the surface tension of the fuel (SFT_F) (c.f. Table 1 and Formula 1). If this is the case, the water, which drains out of the foam, can possess a positive spreading coefficient (S) on the fuel surface.

Formula 1: Definition of the spreading coefficient (S).

$$S = SFT_F - (SFT_A + IFT)$$

- S: spreading coefficient;
SFT_F: surface tension of the fuel;
SFT_A: surface tension of the aqueous phase (the extinguishing agent);
IFT: interfacial tension between the fuel and the aqueous phase.

A positive S is a requirement for the spontaneous spreading of the drainage water of the foam on the fuel surface and the formation of the performance enhancing water film of AFFF. Today all commercially available AFFF include PFS to induce the spreading of their aqueous films. But in the last years we could demonstrated that other classes of surfactants, like siloxane and carbosilane surfactants, can also cause the film formation on the militarily relevant fuels.^{9 10}

A disadvantage of our previously introduced siloxane surfactants, e.g. siloxane surfactant 2 (figure 1), was their complex synthesis. But recently Blunk and Ye from the University of Cologne found a highly efficient method to synthesize the water film forming siloxane surfactant 1.¹¹ This siloxane surfactant is less effective than the previously presented surfactant regarding to

the film formation, but much simpler to synthesize from commercially available starting materials.

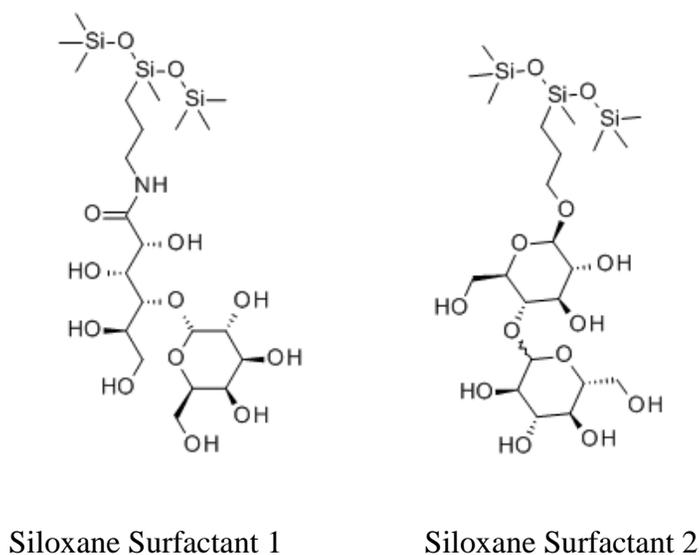


Figure 1: Possible siloxane surfactants for siloxane-based AFFF.

Methods and Materials

The siloxane surfactant 1 was synthesized by us using a slightly modified synthesis method as described by Ye and Blunk.¹¹ The synthesis was scaled up to 1 kg per batch and the purification was simplified from a column chromatography to a filtration. The formation of the desired product and its purity were verified after the filtration process and the removal of the solvent by determination of the critical micelle concentration and NMR-spectroscopy.

The other components of the experimental siloxane-based aqueous film forming concentrate, 2-(2-Butoxyethoxy)ethanol and Glucopon 215 CS UP, were bought from commercial sources and used without further purification. The pH-value of the strongly alkaline alkyl glycoside surfactant Glucopon 215 CS UP was adjusted to 6.6 with 0.037 g Monosodium phosphate per 1.000 g Glucopon before use. After mixing all components of the concentrate together the resulting mixture possessed a pH-value of approximately 7. Then the mixture was filtered through a paper filter to remove unsolved residues.

The 4.6 m²-fire tests were conducted in the fire house of the WIS. These fire tests were realized following a modified ICAO B test protocol,¹² which is described in the German military specification TL 4210-0112.¹³ The only significant modification to the ICAO protocol is the use of the NATO standard fuel F-34 instead of Jet A1. The used F-34 was taken for all extinguishing experiments from the military supply route. For all 4.6 m²-experiments the same foam equipment was used so that an influence of the equipment to the test results was minimized. The 4.6 m²-fire tests were recorded by heat flux sensors (Medtherm Cooperation, Huntsville, Alabama, USA) and a data logger system (Autolog 2005, Peekel Instruments B.V., Rotterdam, The Netherlands). Events like the start of the fire test, the end of the 60 s preburn time and the beginning of the foam application, the 99%-extinguishing time and the 100%-extinguishing time, the end of foam application (60 s after 100%-extinguishing), the start of the burn back experiment (120 s after 100%-extinguishing) were manually marked in the data recording system by pressing a pushbutton.

The 100 m²-fire tests were conducted on the outdoor fire test facility of the WIS. These suppression experiments were carried out in accordance with 100 m²-low expansion foam experiment of the German military specification TL 4210-0112. For the test 2000 l F-34 were given on a bed of 50 m² of water. The foam was produced by a 400 l/min-low expansion nozzle (L4, Total-Walther, Germany) from a premixed solution and smoothly applied on fuel surface over a ramp. The 60 s preburn time, the beginning of the foam application, the 99%-extinguishing time and the 100%-extinguishing time were measured manually using a stopwatch. The complete test was recorded from three different angles by video cameras.

The interfacial and surface tensions were determined with a K100 MK 2 tensiometer (Krüss AG, Hamburg, Germany) using the Wilhelmy-Plate-Method. Cyclohexane (Roth, Germany, p.a.) was used as reference liquid for the measurements of the interfacial tension and the calculation of S.

Results and Discussion

During an extensive test series aqueous film forming solutions of siloxane surfactant 1 were optimized regarding their film formation, interfacial characteristics and foam behavior.¹⁴ The minimum amount of siloxane surfactant 1 was determined by small scale fire suppression experiments and measurements of STF_A and IFT. The foam characteristics of the experimental

solutions were adjusted to the behavior of commercially available fluorine-containing AFFF, which were used as benchmarks. For that reason the co-surfactant Glucopon 215 CS UP and 2-(2-Butoxyethoxy)ethanol were added to the solutions until the solution met the foam behavior of commercial AFFF. Surprisingly siloxane surfactant 1 showed a strong foam formation without any co-surfactants and therefore the amount of co-surfactant could be reduced from 6.8 g/l to 1.8 g/l Glucopon 215 CS UP.

The result of this optimization process was a foam solution, that contains 1.8 g/kg Glucopon 215 CS UP, 1.5 g/kg siloxane surfactant 1 and 5.0 g/kg 2-(2-Butoxyethoxy)ethanol in water. This solution has a spreading coefficient S of 3.1 mN/m and very good results in 4.6 m²-fire suppression experiments with F-34 as fuel (c.f. Table 2).

Table 2: Results of suppression experiments and surface characteristics of a foam solution.

Composition	4.6 m ² -Suppression Experiment			Surface Characteristics		
	Extinguishing Time		25%-Burn Back Time [s]	SFT _A [mN/m]	IFT* [mN/m]	S* [mN/m]
	99% [s]	100% [s]				
	≤ 60	≤ 120	≥ 300			≥ 3.0
1.8 g/kg Glucopon 215 CS UP 1.5 g/kg Siloxane Surfactant 1 5.0 g/kg 2-(2-Butoxyethoxy)ethanol	53	53	570	21.7	0.2	3.1
	48	77	640			

*: with Cyclohexane as reference fuel.

The next step was to generate a firefighting foam concentrate from this experimental foam solution. A 1%- and a 3%-foam agent concentrate were calculated on the basis of the foam solution. Table 3 shows the two calculated concentrates and the content of these components in a typical fluorine-containing AFFF. The comparison of the commercial AFFF and the calculated siloxane-based concentrate demonstrates that the calculated siloxane-based concentrate fits to the expected composition of an AFFF.

Table 3: Composition of a typical fluorine-containing AFFF and two possible compositions of experimental siloxane-based AFFF calculated from the optimized foam solution.

Components	Concentration in a typical 3 vol% AFFF ¹⁵	Components of the Foam Solution		Possible Composition of a Siloxane-based AFFF			
		Ingredients		3 vol%		1 vol%	
	[%]		[g/kg]	[g/kg]	[%]	[g/kg]	[%]
Surfactant (Film Former)	1 – 5 (PFC)	Siloxane Surfactant 1	1,5	50	5	150	15
Surfactant (Foam Former)	1 – 10	Glucopon 215 CS UP	1,8	60	6	180	18
Organic Solvent	15-40	2-(2-Butoxy- ethoxy)- ethanol	5,0	167	17	500	50
Solvent				724	72	170	17

For the further development of the concentrate the temperature limits of the German military specification TL 4210-0112 were used as target range. The TL 4210-0112 defines a temperature range between -15 °C and -60 °C for an AFFF. Surprisingly, it was possible to formulate a 1%-concentrate which gives a stable solution and possess an acceptable viscosity <500 mm²/s within these temperature limits (c.f. Table 4). Because of the possibility to establish a highly effective 1%-concentrate we do not conducted further research on a 3%-concentrate.

After the physical characterization of the experimental concentrate 1%-solutions of this concentrate in tap water were subjected to 4.6 m²-fire tests (c.f. Table 5). In these tests the experimental formulations show a significantly better performance than the tested commercially available PFC-free class-B-foams. Only the fluorine-containing AFFF show slightly better results according to the extinguishing times.

Table 4: Viscosity and density of a concentrate containing 180 g/kg Glucopon 215 CS UP, 150 g/kg Siloxane Surfactant 1, 500 g/kg 2-(2-Butoxyethoxy)ethanol and 170 g/kg solvent.

Temperature [°C]	Viscosity [mm ² /s]	Density [g/ml]
20	61	1.050
0	212	1.065
-15	475	1.075

Table 5: Results of the 4.6 m²-fire suppression tests on the military standard fuel F-34.

Composition	Extinguishing Time [s]		25% Burn Back Time [s]
	99%	100%	
	≤ 60	≤ 120	≥ 300
180 g/kg Glucopon 215 CS UP 150 g/kg Siloxane Surfactant 1 500 g/kg 2-(2-Butoxyethoxy)ethanol 170 g/kg Solvent	55	85	850
	58	90	890
	63	94	860
	59	95	920
Class-B- Foam; 3 vol% solution.	>120	>120	n.d.
	>120	>120	n.d.
AFFF; 3 vol% solution.	42	78	860
	50	75	750

n.d.: not determined.

In addition to the 4.6 m²-tests, 100 m²-fire suppression experiments were conducted with the new 1%-concentrate to confirm the results of the 4.6 m²-experiments. In these tests the experimental concentrate performed better than the no-aqueous film forming fluorine-free class-B-foam and could resist the higher heat flux of the 100 m²-fire (c.f. Table 6). Overall, the new extinguishing foam concentrate met the requirements of the TL 4210-0112 for the 100 m²-fire test.

Table 6: 100 m²-fire suppression experiments with F-34.

Extinguishing Agent	Extinguishing Time		Temperature		Wind [m/s]
	99% [s]	100% [s]	Outside [°C]	Solution [°C]	
Requirement	90	120	0 - 30	10 – 20	≤ 3
Class-B- Foam; 3 vol% solution	100	125	16	16	< 1,5
180 g/kg Glucocon 215 CS UP 150 g/kg Siloxane Surfactant 1 500 g/kg 2-(2-Butoxyethoxy)ethanol 170 g/kg Solvent	75	99	10	11	2,0

Finally a study was launched to clarify the toxicology of the siloxane surfactant 1 and new siloxane-based foam concentrate. This study was necessary because the siloxane surfactant 1 was exclusively synthesized as film former for AFFF and was completely untested.

Table 7: Comparison of some toxicological parameters of the siloxane-based foam concentrate (180 g/kg Glucocon 215 CS UP, 150 g/kg siloxane surfactant 1, 500 g/kg 2-(2-Butoxyethoxy)ethanol and 170 g/kg solvent) and commercial fire extinguishing foams.

Foam Agent	Class-B- Foam	AFFF	Class-A-Foam	Siloxane-based Foam Concentrate
PFC-Content	No	Yes	No	No
Application Concentration on unpolar fuels	3 vol%	3 vol%	1 vol%	1%
German Water Hazard Class 0: no environmental impact; 3: high environmental impact.	1	1	2	1
Fish Toxicity OECD 203 LC ₅₀ [mg/L]	42	~3500	~45	260
Daphnia toxicity OECD 202 EC ₅₀ [mg/L]	644	~700	~45	180
TTC-Test (EN ISO 23753-1)		1:250	1:4000	1:1000
BOD₅ (concentrate) [mg/L]	54 % of COD	70000	405000	800000
COD (concentrate) [mg/L]		580000	1299000	1760000
Degradation OECD 301f after 28 d [%]		72,8	93,5	75.0

The study shows that the siloxane-based foam concentrate possesses a balanced toxicological profile.¹⁶ The new concentrate demonstrates in many points a better environmental behavior than the other commercially available fluorine-free foams if the lower application concentration is taken into account for the siloxane-based foam (c.f. Table 7).

Conclusion

The studied siloxane-based firefighting foam concentrate shows an extinguishing performance which significantly surpasses the commercial PFC-free foams and nearly meets the performance of the PFC-containing AFFF in the fire suppression tests with the NATO standard fuel F-34. The viscosity and density of the highly effective 1%-concentrate are acceptable in a temperature range between -15 °C and 60 °C. Finally the toxicological behavior of the experimental foam concentrate is acceptable.

In summary, we can state that siloxane-based PFC-free AFFF are easily manufactured and perform significantly better on F-34 than the non-aqueous film form class-B-foam without persistent ingredients.

Outlook

Concluding a study for the decomposition of the siloxane backbone is planned for near future to investigate the complete degradation process of the aqueous film forming siloxane surfactants.

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