Fire Testing of Experimental Siloxane-Based AFFF: Results from New Experiments

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Introduction

Aqueous film forming foams (AFFF) are the most effective fire extinguishing agents for pool fires but hitherto these foams possessed a severe disadvantage, which is their adverse environmental impact.[1] For the formation of the eponymous water film AFFF imperatively contain ecologically problematic polyfluorinated compounds (PFC) which are persistent in nature. Their resistance to biodegradation leads to serious restrictions for the use and the disposal of AFFF in Germany and other countries. As consequence of the environmental problems the Bundeswehr (German Armed Forces) is strongly interested in a replacement of the PFC in AFFF by a more environmentally sound class of surfactants.

Theoretical Background

The water film of AFFF can spread spontaneously on the surface of a liquid fuel only if the spreading coefficient (S) is positive. S is defined as the difference between the surface tension of the fuel (SFT_F) and the sum of the surface tension of the aqueous phase (the extinguishing agent, SFT_A) and the interfacial tension between the fuel and the aqueous phase (IFT), cf. Formula 1.

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

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

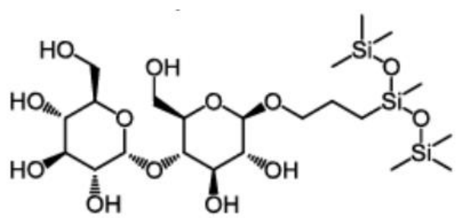
Today all commercially available AFFF establish $S > 0$ by PFC, these high performance surfactants are indispensable to establish a significantly lower SFT_A than the SFT_F.

Table 1: Surface tensions of militarily important fuels.

	Fuel	SFT_F (24 °C)	Sample Origin
1	Diesel	28.3 mN/m	BP Refinery Emsland, Germany
2	Jet fuel	26.7 mN/m	BP Refinery Emsland, Germany
3	F-34	25.8 mN/m	Bundeswehr (NATO Standard Fuel[2])
4	Cyclohexane	24.9 mN/m	Reference substance, Sigma-Aldrich

Table 1 shows the SFT_F of some military relevant fuels and Cyclohexane. Cyclohexane was added to this list because of its importance as reference substance for film forming experiments and measurement of the IFT. Cyclohexane was chosen for this purpose because it possesses a determinate composition, a slightly lower surface tension than the militarily interesting fuels and a flashpoint above room temperature. Using Cyclohexane the existence of a vapor-tight water film, which is formed on the fuel surface by a surfactant solution, can be tested under reproducible conditions by a simple pilot flame, which is guided some millimeters above the fuel layer. Based on interfacial activity data and film forming experiments on Cyclohexane and F-34 several high performance siloxane and carbosilane surfactants were identified as possible, environmentally sound film formers for PFC-free AFFF.[3 4 5]

Current Developments



T-C3-Malt

Figure 1: The water film forming siloxane surfactant, T-C3-Malt.

While working on this project more than 250 siloxane and carbosilane surfactants were synthesized and tested as possible film formers for PFC-free AFFF. From this multiplicity of compounds the siloxane surfactant T-C3-Malt (Figure 1) was chosen for a fire test series because of its film forming ability and foaming behavior.

Table 2: Surface and interfacial characteristics as well as film formation properties of siloxane T-C3-Malt solutions.

	Chemical Composition	SFT_A [mN/m]	$IFT^{\#}$ [mN/m]	$S^{\#}$ [mN/m]	Film on Cyclohexane	Film on F-34
1	6.8 g/l Glucopon 215 CS UP 2.5 g/l 2-(2-Butoxyethoxy)ethanol	28.5	1.0	- 4.5	No	No
2	6.8 g/l Glucopon 215 CS UP 2.5 g/l 2-(2-Butoxyethoxy)ethanol 0.25 g/l T-C3-Malt	25.8	0.8	- 1.6	No	Yes*
3	6.8 g/l Glucopon 215 CS UP 2.5 g/l 2-(2-Butoxyethoxy)ethanol 0.50 g/l T-C3-Malt	24.1	0.7	0.2	Yes	Yes
4	6.8 g/l Glucopon 215 CS UP 2.5 g/l 2-(2-Butoxyethoxy)ethanol 1.00 g/l T-C3-Malt	23.5	0.5	1.0	Yes	Yes
5	6.8 g/l Glucopon 215 CS UP 2.5 g/l 2-(2-Butoxyethoxy)ethanol 2.00 g/l T-C3-Malt	22.2	0.4	2.4	Yes	Yes

#: based on Cyclohexane (SFT_F=25.0 mN/m);
*: small area film formation, recontracting after a short term.

Solutions of T-C3-Malt with concentrations above approximately 0.5 g/l T-C3-Malt in Water with 6.8 g/l Glucopon 215 CS UP (Glucopon) and 2.5 g/l 2-(2-Butoxyethoxy)ethanol as additional components show a positive spreading coefficient and a water film formation on Cyclohexane und F-34 (cf. Table 2).

In addition to the tabulated interfacial characteristics the foam behavior of the T-C3-Malt-containing solutions was determined. For comparability reasons all fire and foam tests were carried out with the same foaming device. A so-called Micro Foam Unit (M.F.U. V-25, Jürgen Arens, Production and Distribution of Instructional Media, Cologne, Germany) with a low expansion nozzle (also Jürgen Arens) was used for the expansion of all foam solutions. The nozzle was operated with a working pressure of 4.5 bar and a discharge rate of 1.06 kg/min.

Expansion and drainage times were measured in a graduated glass cylinder (2000 ml nominal volume, 2330 ml gravimetric determined total volume, 7.9 cm diameter). An electronic balance was placed under the glass cylinder to determine gravimetrically the applied quantity of foam solution. The expansion was calculated from the total volume of the cylinder, the weight and the density of the foamed solution. The 50%-drainage time was measured using the graduation of the glass cylinder.

The data of the foaming experiments is summarized in Table 3. The results show that the content of T-C3-Malt does not affect the expansion and the 50%-drainage time on a larger scale. Only minor positive effects of T-C3-Malt are visible in both cases.

Table 3: Foam characteristics of siloxane surfactant solutions.

	Chemical Composition	Expansion Factor	50%-Drainage Time [min]
1	6.8 g/l Glucopon 215 CS UP 2.5 g/l 2-(2-Butoxyethoxy)ethanol	10.66 ± 0.16	05:39 ± 0:03
2	6.8 g/l Glucopon 215 CS UP 2.5 g/l 2-(2-Butoxyethoxy)ethanol 0.25 g/l T-C3-Malt	10.76 ± 0.08	5:44 ± 0:02
3	6.8 g/l Glucopon 215 CS UP 2.5 g/l 2-(2-Butoxyethoxy)ethanol 0.50 g/l T-C3-Malt	10.89 ± 0.15	5:36 ± 0:02
4	6.8 g/l Glucopon 215 CS UP 2.5 g/l 2-(2-Butoxyethoxy)ethanol 1.0 g/l T-C3-Malt	10.80 ± 0.09	6:00 ± 0:05
5	6.8 g/l Glucopon 215 CS UP 2.5 g/l 2-(2-Butoxyethoxy)ethanol 2.00 g/l T-C3-Malt	10.88 ± 0.11	6:05 ± 0:03

In the fire test series four different application rates were studied for each foam solution and commercial firefighting foam. For the experiments two round fire pans in accordance to EN 3-7 were used, 55B (application rates 0.8 – 1.8 kg/min×m²) and 21B (application rates

> 1.8 kg/min×m²). To realize the different application rates with only one low expansion nozzle the burning area of the fire pans was varied by a stainless steel tape, which was bent to a ring and adjusted to the required area and diameter with two steel clamps. For each fire test this ring was placed concentrically in the fire pan which was filled with a 3.0 cm water layer. Then the fuel was carefully filled in the inner ring. The fuel quantity was dependent of the desired burning area and application rate (from 5 l at 3.0 kg/min/m² up to 21 l at 1.0 kg/min/m²). During the fire test the foam was smoothly given on the burning fuel surface by a ramp, which was set on the edge of the ring. The 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.

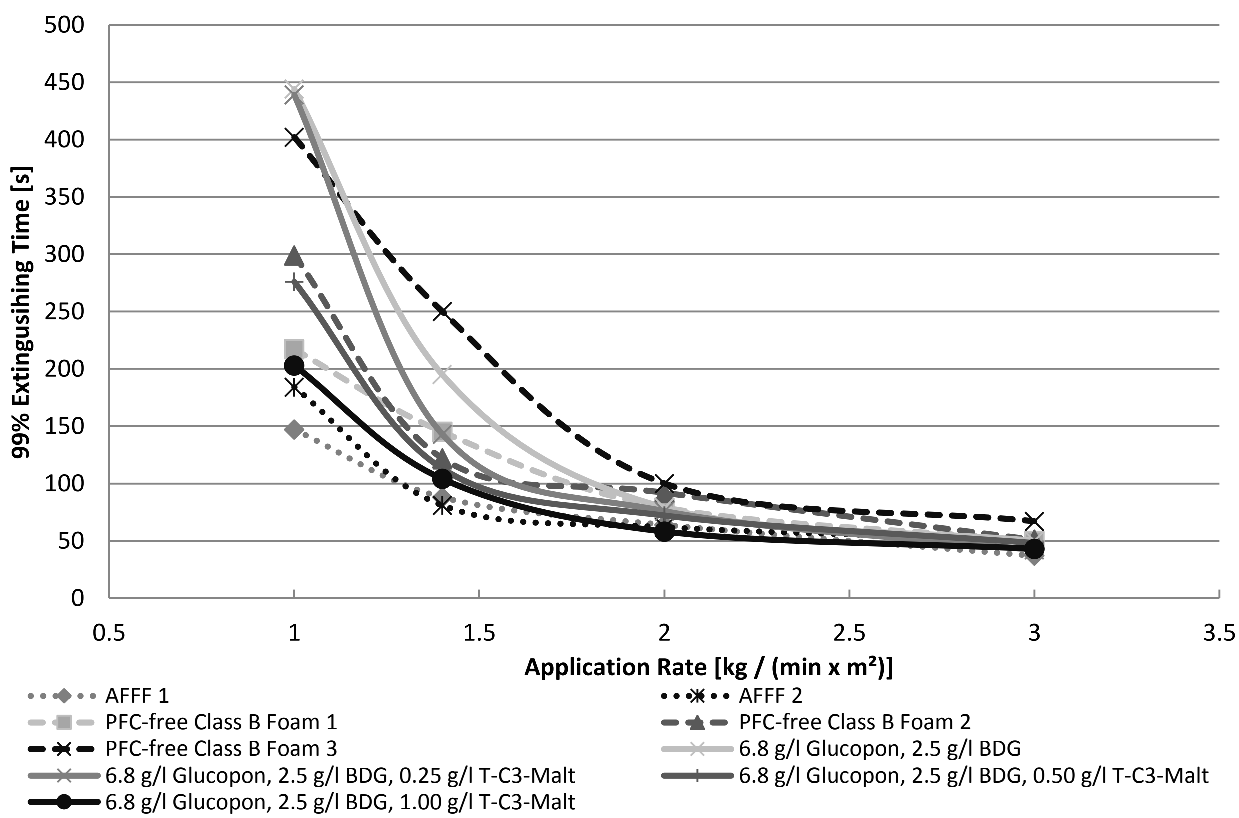


Figure 2: Comparison of the 99%-extinguishing times of siloxane surfactant solutions and commercial firefighting foams.

Throughout the fire test series the concentration of the siloxane surfactant was varied like in the case of the foam and interfacial experiments; all other components of the experimental foam mixture and all other variables, e.g. the low expansion nozzle, the working pressure of the foaming device, were held constant to demonstrate exclusively the influence of the siloxane surfactant concentration.

The series of fire tests shows that the rising of the siloxane surfactant concentration strongly reduces the fire extinguishing times on F-34 (cf. Figure 2 and Figure 3). In comparison with commercially available fluorine-free Class B foams and AFFF, according to the German Armed Forces technical specification TL 4210-0112, the experimental siloxane based aqueous film forming foams clearly surpass the fluorine-free Class B foams and reach nearly the extinguishing performance of the environmentally problematic and PFC containing AFFF (cf. Figure 2 and Figure 3).

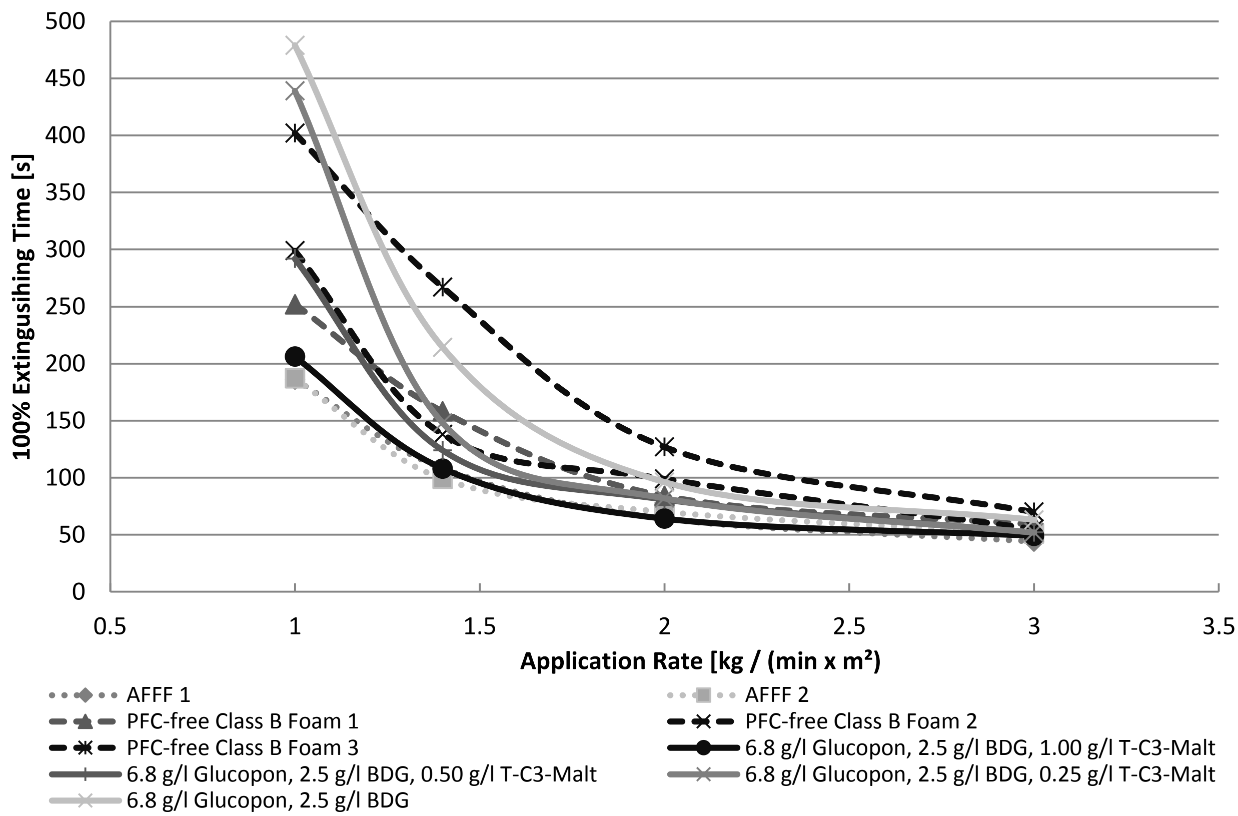


Figure 3: Comparison of the 100%-extinguishing times of the surfactant solutions and various firefighting foams.

Because of the complex synthesis and the limited supply of T-C3-Malt, the foam solution with 2.00 g/l T-C3-Malt could not be fire tested. But it is to be expected, that the extinguishing performance still increases further in comparison to the solutions with a lower siloxane concentration because of the observed interfacial data for this concentration.

Recently, a new short synthesis with excellent yield was found for a new film forming siloxane surfactant. Due to this synthesis and because of the thereby available amount of surfactant it is now possible to conduct standardized fire tests according to the 2013 updated ICAO fire test protocol.[6] Table 4 shows the results of ICAO B tests performed with two different foam solutions of the new siloxane surfactant and AFFF according to TL 4210-0112 as benchmarks.

Table 4: Results of ICAO B fire tests with a new siloxane surfactant.

Type of Foam Solution	Chemical Composition / Commercial Foam	Extinguishing Time [s]		25%-Burn Back Time [s]
		99%	100%	
Requirements		**≤ 60**	**≤ 120**	**≥ 300**
PFC-free siloxane based foam solution	6.8 g/l Glucopon 215 CS UP 2.5 g/l 2-(2-Butoxyethoxy)ethanol 2.0 g/l new siloxane surfactant	42	70	641
		45	66	660
	6.8 g/l Glucopon 215 CS UP 2.5 g/l 2-(2-Butoxyethoxy)ethanol 2.0 g/l new siloxane surfactant 0.15 g/l Xanthan gum	45	60	n.d.
		47	60	n.d.
PFC-containing AFFF according to TL 4210-0112	AFFF 1	59	88	573
		53	98	604
	AFFF 2	41	87	756
		43	82	779
	AFFF 3	42	78	863
		50	75	752

The foam solutions containing the new siloxane surfactant completely achieve the requirements of the ICAO B test protocol. In comparison to the classic AFFF the experimental solutions reach already the extinguishing performance and nearly the burn back stability of the PFC-loaded high performance firefighting foams.

Conclusion

The present study shows that water film forming siloxane surfactants can significantly increase the extinguishing performance of firefighting foams. It could be proved that foams containing these compounds in a sufficient concentration surpass already the PFC-free Class B foams and reach nearly the performance of classic AFFF in small scale fire tests. In the standardized ICAO B fire test a new and easily available siloxane surfactant demonstrated that solutions of this surfactant can easily achieve the requirements of the ICAO B level. Furthermore these foams meet the excellent extinguishing performance of the classic AFFF involving the ecologically undesired PFC.

Summarizing, it can be stated that the conducted experiments show the ability of siloxane surfactants to act as an alternative film forming compound for PFC-free high performance firefighting foams for pool fires.

Outlook

Further fire tests according to international standards, e.g. ICAO B and C, are scheduled. Additionally, a long-term storable concentrate should be developed based on the experimental siloxane solutions.

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