A fluorine-free future for AFFF?

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Introduction

Today the most efficient agent to extinguish liquid fires is AFFF (aqueous film forming foam). In the last ten years the use of this agent is increasingly restricted because of the contained persistent fluorosurfactants.[1] [2] Especially for the Bundeswehr (German Armed Forces) these environmental problems are strengthened by the fact that a prepared effective fire fighting water retention is not possible in every case. Examples for this situation are the applications of AFFF on airfields in the country of deployment or aboard ships. In consciousness of these environmental problems the Bundeswehr Research Institute for Protective Technologies has been working on the reduction of fluorine-compounds in AFFF for the last two decades. Since 2010 we have been researching on the development of a fluorine-free AFFF.

Table 1: Important liquid fuels.

	Fuel	SFT_{Fuel} (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[3])
5.	Ethanol	22,2 mN/m	BP Refinery Emsland, Germany
6.	Gasoline	20,7 mN/m	BP Refinery Emsland, Germany
7.	Cyclohexan	24,9 mN/m	Reference substance, Sigma-Aldrich

Basics

In order to generate an aqueous film on a fuel surface, a positive spreading coefficient (S) is needed. S is positive, if the surface tension of the fuel (SFT_{Fuel}) is higher than the sum of the surface tension of the foam solution (SFT_{Foam}) and the interfacial tension between the foam solution and the fuel (IFT).[4]

$$S=SFT_{Fuel}-(SFT_{Foam}+IFT).$$

Table 2: Performance of several surfactant types.

	Surfactant Type	Minimum SFT_{Foam} (aqueous solution; 20 °C)	Comment
1.	Fluorosurfactants	15 mN/m	
2.	Siloxane surfactants	20 mN/m	
3.	Carbosilane surfactants	23 mN/m	
4.	Alkyl surfactants	28 mN/m	
5.	no surfactant	73 mN/m	pure water

So far a positive spreading coefficient of an AFFF is only possible by the use of fluorosurfactants. But there is the theoretic possibility of a positive coefficient S on important liquid fuels (Table 1) by the use of high performance siloxane surfactants (Table 2). Especially for military relevant fuels like F-34, Diesel and Jet Fuel exists a good chance to find a siloxane-based AFFF. According to this fact we have been focusing our work on a fluorine-free AFFF for liquid fuels with a SFT_{Fuel} >25mN/m (Table 2). For that reason Cyclohexane ($c\text{-}C_6H_{12}$) is used as reference liquid for film forming experiments. In the next chapter the search for suitable siloxane surfactant based AFFF is reported.

Current developments

At the beginning of the project we checked the commercial obtainable siloxane surfactants as film forming surfactant. After a short time literature research and experiments showed that aqueous solutions of these compounds don't form a water film on $c\text{-}C_6H_{12}$. We were forced to synthesize the needed surfactants by ourselves. In cooperation with the research group of Dirk Blunk (Department of Organic Chemistry; Universtity of Cologne) we synthesized and characterized over 30 siloxane surfactants in the last two years. (Table 3 shows some examples of our siloxanes.) Only one third of the proven surfactants forms aqueous films on $c\text{-}C_6H_{12}$. But finally we identified lead structures which are related to the film formation on liquid fuel.

Table 3: Data of several siloxane surfactants in aqueous solution.

Surfactant	Concentration [mg/L]	SFT [mN/m]	IFT to $c\text{-}C_6H_{12}$ [mN/m]	$S^{\#}$ [mN/m]	Aqueous Film on $c\text{-}C_6H_{12}$
Ethoxy-Siloxane	500	20,6	0,5	3,9	No
BuM14	10188	20,3	2,5	2,2	No
BuM20	10134	20,7	1,2	2,1	No
BuM21	10194	21,2	1,4	2,4	No
KAWI 202	184	20,4	7,9	-3,3	No
KAWI 206	303	21,0	4,1	-0,1	No
KAWI 211	541	20,8	3,8	0,4	No
KAWI 212	126	20,4	9,3	-4,7	No
KASE 017	247	21,3	0,4	3,3	Yes
KASE 018	503	20,2	0,1	4,7	Yes
RH-77	502	20,2	0,1	4,7	Yes

$^{\#}$ calculated with a SFT of 25 mN/m for $c\text{-}C_6H_{12}$.

Our manufactured surfactants and conducted formulation experiments show that a siloxane based AFFF is very likely possible. Several suitable surfactants were identified, which can cause the formation of aqueous films on a fuel surface (table 3).
Experimental foam concentrates build by some of these siloxane surfactants are already tested. In a 3% solution they possess an appropriate expansion for low-expansion foam, a positive spreading coefficient and form an aqueous film on fuel. As fuels were cyclohexane ($c\text{-}C_6H_{12}$) and the NATO

standard fuel F-34 tested. The results of these tests make us confident that the planned fluorine-free AFFF is possible. The Surfactants RH-77 and KASE 018 were already manufactured for further experiments in amounts of up to 100 g.

Actual, only one experimental formulation was subjected to fire tests (table 4). The extinguishing times of our siloxane-based formulations are within the expected range. The extinguishing times of the siloxane-based formulations are near to a fluorine-containing AFFF and substantial shorter than the times of fluorine-free Class B Foams.

Table 4: Micro Fire Tests (test pan: 0,66 m² round; application rate: 1,1 L/min; fuel: 7,0 L F-34; buffer: 10,0 L water; preburn time: 0 s).

	Foam Concentrate	Extinguishing Time	Fluorine	Siloxane	Comment
1.	Siloxane-based AFFF	2:04	No	Yes	Siloxane: KASE 018
2.	Siloxane-based AFFF	3:30	No	Yes	Siloxane: KASE 018 (½ amount of siloxane)
3.	Benchmark AFFF	1:16 min	Yes	n.d.	
4.	Benchmark Class B Foam	> 6:00 min	No	n.d.	Not extinguished!

The results encourage us that our proposed way could lead us to success. But it was only a first small series of tests and the experiments were conducted outside. So influences of wind and temperature are possible. This year, a larger indoor fire test series is planned to ensure these results.

Outlook

The encouraging results lead us to the primary goal for 2012: The statistical verification of the fire tests. After demonstrating the effectiveness of siloxane-based AFFF in principle we will focus on the advancement of our foam formulation. According to the film and storage stability of the experimental foam formulations there is still a lot of work to be done.

After these tests the simplification of the siloxane surfactant synthesis is an important point. Today our best siloxane surfactants are prepared in a four step synthesis. So there is a need to reduce the effort and the costs of this synthesis, if we want to produce a large amount of material for final large scale fire tests.

Finally the environmental behaviour of the siloxane surfactants and their dismantling in the environment have to be completely cleared up, in order to exclude future risks for nature and user.

[1] European Union, (2006) DIRECTIVE 2006/122/ECOF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL. European Union, Brussels.
[2] UNEP, (2009) STOCKHOLM CONVENTION ON PERSISTENT ORGANIC POLLUTANTS -ANNEX B.
[3] NATO, (1997) Logistics Handbook. NATO, Brussels.
[4] Alan L. Woodman, Herbert P. Richter, Arnold Adicoff, Alvin S. Gordon; Fire Technology **1978;** 265-272.