

THE ENVIRONMENTAL IMPACTS OF FIRE-FIGHTING FOAMS

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Abstract

Extinguishing foams are commonly used for extinguishing the fire of flammable liquids, whereby their insulating, choking and quenching effects are exploited. The purpose of the paper is to consider and compare the foams currently used in fire departments, regarding mainly their high extinguishing effect (capability of faster aborted burning on the large surface at low foam consumption), but also their impact on the environment in each stage of their life cycle.

Key words

Foams, fire extinguisher, fire

Introduction

Extinguishing agents are various substances and materials used for stopping (slowing down) the combustion process. Basic requirements for extinguishing agents are as follows:

- they must have high extinguishing effect (the ability to quickly stop the burning of large areas at low consumption),
- they must not be harmful to human (living) organisms when both their used and stored,
- they must be available at reasonable price, and others.

Fire-fighting foams play a significant role as extinguishing agents.

Characteristics of fire fighting foams

Fire-fighting foam is an extinguishing agent composed of numerous bubbles formed mechanically or chemically from liquid. Chemical foam is formed by the reaction of alkaline solution with acidic solution in the presence of the foam stabilizer. Mechanical foam is formed after introducing the air and/or inert gas into a foaming solution [1].

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Foams belong to the two-phase disperse systems consisting of dispersive media (liquid) with a dispersed phase - three-dimensional lamellae of permanent structure containing enclosed gas. Plate thickness ranges from 0.001 to 0.01 mm [2].

Foam fire effects consist of the following physical principles (Figure 1):

- Isolation - separate flammable substance from flame,
- Choky - prevents access of air oxygen to flammable substance, prevents the evaporation of flammable liquids,
- Refrigerating - reduces the temperature of the burning substance and thus slows down burning, which is directly proportional to the water content in the foam [3].

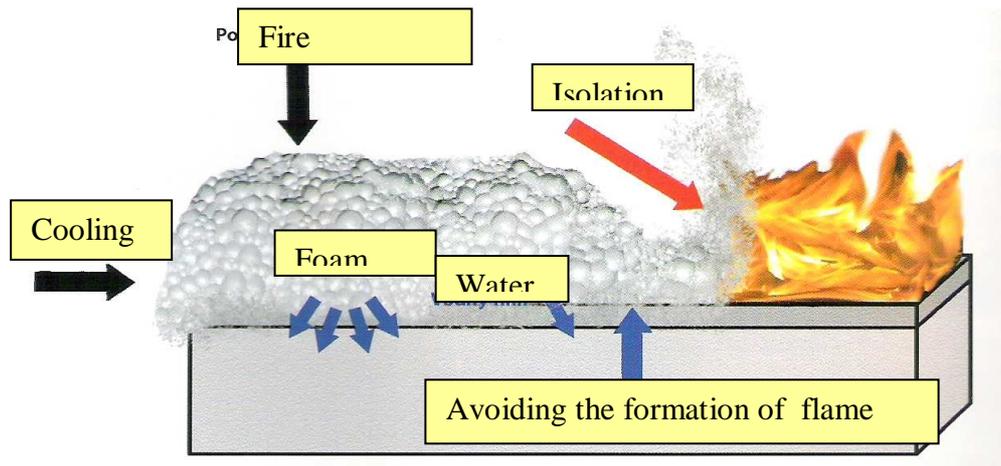


Fig. 1 Scheme of the extinguishing mechanism by using foam [3]

Fire-fighting foams are commonly used to reduce the spread and extinguishing of Class B fires and to prevent re-ignition. These foams can be used to prevent ignition of flammable liquids and in certain conditions for extinguishing Class A fires. Foams can be used in combination with other extinctive substances, mainly gaseous and powder ones [4].

The first foam fire extinguishers worked on a principle of chemical foam. Currently, an air-mechanical foam or the foam which is formed at the moment of the contact of a given foaming agents with fire are being developed. [3].

Air-mechanical foam is prepared at the time of the intervention of a mechanical mixture of solution consisting of water and a foaming solution with atmospheric air in a foaming nozzle. Foaming solution arises in the mixer by injector sucking the foamer into the water. Foamer concentration in water usually ranges from 1 % to 6 %. Gas component can also be carbon dioxide, nitrogen or another inert gas [2].

Physical properties of foamers

Foamer is a liquid mixed with water in a prescribed concentration to give a foaming solution. Foam is a dispersion system where dispersing agent is gas (air) and dispersive environment is liquid (heterogeneous mixture of gas and liquids). It is an unstable system subject to rapid change. Foam is a cluster of air bubbles generated from a foaming solution. The speed of this transformation is important for assessing the stability of the foam [1]. Stability properties as well as the effectiveness of foam and foamers are determined by their

physical and chemical properties. The monitored physical and chemical properties of foamers and foams include:

- **Number of foaming** - the ratio of volume of produced foam to the volume of liquid, by which was this foam produced. This number indicates how many times the volume of foam is larger than the volume of foaming solution. Based on this number, foams are divided into three groups (severe, moderate and light foams),
- **Viscosity** - is an expression of fluidity of liquid, it depends on temperature (decreases with increasing temperature),
- **Foamer frost resistance** - the temperature at which the substance is liquid and does not begin to exclude solid parts,
- **Content of the sediment** - the proportion of solid components in concentrates of foamers expressed in % vol.,
- **Foam stability** - is influenced by excretion of water from the foam, defined by half-life, respectively quarter-life, which is the time required to eliminate a half, respectively a fourth of water contained in the foam [1],
- **Half-life of foam** - the time at which the foam releases 50 % of foaming solution, given in minutes. The conversion speed is an important determinant of quality and stability of foam,
- **pH** - liquid reaction, i.e. acidity, alkalinity or neutrality expressed as the negative decimal logarithm of hydrogen ion activity,
- **A foaming solution spreading factor** - a measure that indicates the ability of one liquid to unfold spontaneously on the surface of another liquid; it is not an indicator of its quality; it is given in $\text{mM}\cdot\text{m}^{-1}$ [3].

Stability of foams depends on the structure of surface films from the so-called foaming agents such as electrolytes, soaps, saponins, proteins, etc. In the process of fire fighting, the foams are constantly disrupted by the influence of heat of ignition, internal force of foam and hot surface of burning liquid. It is proved that the degradation rate of foam by flame heat effect is much smaller than on the actual surface of the heated evaporating liquid. In this process, foams have insulating and cooling effect. These effects depend on the type and quality of used foamers. More factors influence the quality; from a practical point of view, important are conditions and storage period of foams [6, 7].

Foam as the extinguishing substance is prepared at the time of intervention. Properties of foam and its quality are affected by the properties and purity of the used chemicals, i.e. water, foaming agents and gas component (usually air). Used foaming equipment has also a significant impact on the quality of foam.

Knowing the nature and application of particular foaming agents, it is possible to prepare foam at the moment of an instant action, regarding to particular fire. As for composition and the resulting properties, foamings are divided into the following groups [5]:

- Protein foamers (P),
- Fluorine-protein foamers (FP),
- Synthetic foamers (S),
- Alcohol resistant foamers (AR),
- Aqueous film forming foamers (AFFF),
- Fluorine-protein foamers forming a water film (FFFP) [4, 6].

Extinguishing properties of foamers are summarised in Table 1.

NORMAL FIRE FIGHTING CAPABILITIES OF DIFFERENT TYPES OF FOAMERS [4]

Table 1

Type of foamer	Extinguishing Class ability	Level of resistance to re-burn	Film-forming
AFFF (no AR)	I	C	+
AFFF (AR)	I	B	+
FFFP (no AR)	I	B	+
FFFP (AR)	I	A	+
FP (no AR)	II	A	-
FP (AR)	II	A	-
P (no AR)	III	B	-
P (AR)	III	B	-
S (no AR)	III	C	-
S (AR)	III	C	-

Storage of foamers

One of the major factors affecting the properties of foamers and foams is their storage life. If foamers are stored in their original packaging according to the manufacturer's instructions, they are applicable for several years without the change in their original characteristics. However, if a mixture of foamer and water (foaming solution) is ready for frothing and is located in the piping system or in vehicle tank, it must be changed each year.

Synthetic foamers must be stored in a container made of stainless steel or plastic. Protein foamers are stored in steel and metal containers. Zinc, tin or aluminium containers are not suitable for storage, as foamers are very aggressive and attack these materials.

Valves, pumps and tanks for storage of foamers must be made of the same type of metal. In case of contact of different types of metals, foamers would cause electrochemical corrosion. Foamers are very sensitive to temperature changes. Optimal temperatures are in the range +5 to +25°C. Negative effects on foamers' properties were not observed even in the temperature range 15 to + 40 °C. After re-thawing, foamers can be re-used since there are no changes to their basic physical and chemical properties and no reduction of their fire fighting effectiveness [3].

Foamers' impact on environment

The products of combustion and the combustion residues are much more harmful than the extinguisher used. Quickly extinguished fire often outweighs the negative impacts of the extinguishing agent by reducing the formation of toxic products and residues after burning. When extinguishing fires for example by water which is considered to be harmless to environment, the effluent water contaminated by decomposed products of combustion may significantly pollute the environment in a long time horizon. Fires can be extinguished much faster by applying the fire fighting foams which are environmentally acceptable by posing less pollution to the environment.

Environmentally acceptable fire fighting foams should have at least the same fire fighting capability as traditional foams made of protein or AFFF foamers with minimal environmental impact (water, soil). Traditional ingredients in foamers (tensides, ethylene glycol, butyldiglycol, propylene glycol, alkylpolyglycoside, nonylalcohol) are known to cause problems in terms of toxicity of the substances themselves, respectively their degradation products. Fish and aquatic organisms are highly endangered by the application of fire fighting foams. Though when compared with chemical substances and preparations, toxicity of foamer is low, some problems arise due to the secondary toxicity resulting from the long biodegradability of decomposition products in the environment.

Biodegradability of foamers means their ability to degrade by biological or chemical ways the original substance to decomposition products environmentally acceptable, for example by assimilation (water and carbon dioxide). Biological degradation is caused by microorganisms and fungi. Foamer degree of degradation is often given as the ratio of biochemical oxygen demand (BOD) and chemical oxygen demand (COD).

Biochemical oxygen demand is the amount of dissolved oxygen consumed by microorganisms over time, e. g. 5 days (BOD₅) in the biochemical processes of decomposition of organic substances in water under aerobic conditions. This quantity of oxygen is proportional to the quantity of present degradable organic substances and it can be therefore estimated from the BOD level of water pollution by extinguishing foam. Biochemical oxygen demand is determined in the original or a suitably diluted solution of foamer.

Chemical oxygen demand represents the amount of oxygen required for oxidation of organic substances in water using strong oxidants over time (usually two hours). It is the rate of total organic substances in water and thus an indicator of organic pollution of water.

Biodegradability of foamer is expressed as a ratio of COD and BOD₅ in percentage (%) biodegradation:

$$\text{BOD}_5/\text{COD} \quad (1)$$

Ideal foam should have a full-degradability and should not significantly consume dissolved oxygen in water. Environmentally friendly foam (i.e. Green foams) should extinguish fires as effectively as traditionally used foams, but we have to know their degradation, otherwise no significance. They are several times more expensive than conventional foams, but on the other hand, their extinguishing capacity may several times exceed that of the fluorine-protein and AFFF foams (good quenching of the flames in AFFF and prevention of re-overing typical for fluorine-protein foams).

EXPERIMENTAL

The aim of the experiment was to assess the extinguishing properties of foamers in the laboratory and then experimentally verify their impact on the environment. The following measurements were therefore made:

- monitoring the numbers frothing and foaming time,
- determining the half-life,
- determining viscosity,
- determining the biochemical and chemical oxygen consumption,
- carrying out ecotoxicological tests on higher plants.

The following foamers were used in the experiment (Table. 2):

USED FOAMERS AND THEIR CHARACTERISTICS

Table 2

Name of foamer	Producer	Use for Classes of fires	Recommended concentration	Notes
Sthamex AFFF 1 %	Fabrik chemischer Präparate von Dr. Richard Sthamer GmbH & Co.KG, Hamburg, Germany	A a B	1 %.	pecially designed for hydrocarbon fires, plastics and mineral oil products
Sthamex AFFF F-15	Fabrik chemischer Präparate von Dr. Richard Sthamer GmbH & Co.KG, Hamburg, Germany	A a B	3 %.	Specially designed for fires of oil products and plastics
Pyronil	Chemtura Corporation, USA	A a B	3 %	synthetic multipurpose foamer, also light foam
Moussol APS F-15	Výrobca: Fabrik chemischer Präparate von Dr. Richard Sthamer GmbH & Co.KG, Hamburg, Germany	A a B	3 %	fire fighting of liquid of non-polar hydrocarbons
			6 %	fire fighting of liquid of polar hydrocarbons

Their selection was based on the research findings available in HZZ. Foamers were prepared in five different concentrations (1 %, 3 %, 6 %, 9 % and 12 %).

I. ASSESSMENT OF FOAMERS IN TERM OF EXTINGTIVE AND PHYSICAL PROPERTIES

Number of foaming

The number of foaming (E) was determined in accordance with STN EN 1568-3: 2002 standard Technical conditions of foamers for heavy foams for the surface use with the liquid immiscible with water. Determined was the number of frothing of selected foamers of different concentrations, and the time of foam formation (Table 3).

NUMBER OF FROTHING AND TIME OF FOAMING TESTED FOAMERS

Table 3

No	Concentration of foamer [%]	Number of frothing E				Time of foaming [s]			
		Sthamex AFFF 1 %	Sthamex AFFF F-15	Pyronil 1	Moussol APS F-15	Sthamex AFFF 1 %	Sthamex AFFF F-15	Pyronil	Moussol APS F-15
1.	12	4.886	4.909	4.901	4.822	6.61	16.58	17.71	19.23
2.	9	4.894	4.891	4.908	4.854	11.69	19.20	20.34	23.38
3.	6	4.890	4.827	4.878	4.887	13.35	19.25	25.63	26.20
4.	3	4.906	4.826	4.839	4.837	14.70	25.28	30.55	30.24
5.	1	4.827	4.883	4.820	4.807	27.35	35.04	34.44	57.81

Number of frothing ranged around the value 4.9 ± 0.1 for all foamers, allowing a fair comparison foaming time. The fastest foamed foamers Sthamex AFFF 1%, AFFF Sthamex F-15, then Pyronil and the longest foaming time had Moussol APS F-15, in which time foaming at 1% concentration significantly extended.

Half-life

Regarding the manufacturer recommendations in the safety data sheets, half-life was tested by using 3% solutions while monitoring the time in which 50% of the foaming solution was released from the foam. The results of the measured values for each foamer are given in Table 4.

HALF-LIFE OF TESTED FOAMERS (3 % solutions) Table 4

No	Name of foamer	Half-life [s]
1.	Sthamex AFFF 1 %	62
2.	Sthamex AFFF F-15	166
3.	Pyronil	187
4.	Moussol APS F-15	187

The most favorable results were achieved by using Pyronil and Moussa APS F-15 foamers, where the half-life was 187 seconds.

Measurement of foamer viscosity

Viscosity was determined according to DIN 53015:2001 Viscometry - Measurement of viscosity using the Hoespler falling-ball viscometer for viscosity, etri Höppler KF 3.2, which is designed primarily to measure the dynamic viscosity of Newton's liquids. It measured the time of a ball fall between two lines, and the calculation of the viscosity was calculated from the relation:

$$\eta = t.(\rho_1 - \rho_2).K, \quad (2)$$

where

- η the dynamic viscosity in mPa.s,
- t fall time of balls in s,
- ρ_1 ball density in g.cm^{-3} ,
- ρ_2 density of the fluid in the bath temperature g.cm^{-3} ,
- K the constant $\text{mPa.cm}^3.\text{g}^{-1}$

The results are shown in Table 5.

MEASUREMENT RESULTS OF FOAMER VISCOSITY Table 5

No	Name of foamer	t [s]	ρ_1 [g.cm^{-3}]	ρ_2 [g.cm^{-3}]	K [$\text{mPa.cm}^3.\text{g}^{-1}$]	η [mPa.s]
1.	Sthamex AFFF 1 %	124	2.224	1.07	0.07293	10.436
2.	Sthamex AFFF F-15	70	2.224	1.04	0.07293	6.044
3.	Pyronil	76	2.224	1.545	0.07293	3.466
4.	Moussol APS F-15	69	8.142	1.170	0.1225	58.931

The lowest viscosity was measured in Pyronil a Sthamex AFFF F-15 foamers, the highest in Moussol APS F-15.

II. FOAMER IMPACT ON THE ENVIRONMENT

Determination of biochemical oxygen consumption

The basis of the test is the treatment and dilution of water sample to be analyzed by different amounts of diluent water with a high amount of dissolved oxygen and vaccinic aerobic microorganisms with prevention of nitrification. Incubation was conducted at 20 °C within a defined time of 5 days in the dark in a full closed flask. The dissolved oxygen concentration was determined before and after incubation according to STN EN 1899-1 Water quality - Determination of biochemical oxygen consumption after n days (BSKn): Part 1: Dilution and inoculation method with the addition of allylurea. Used was vaccinated diluting water, and dissolved oxygen was electrochemically determined (Table 6).

Determination of chemical oxygen consumption

The oxidizable substances in the test sample volume were oxidized by a known quantity of potassium dichromate in the presence of mercuric sulphate and silver catalyst in an environment of concentrated sulphuric acid in a defined time interval. COD value was calculated based on the amount of reduced dichromate. The COD indicator shows the total content of organic substances in water - organic water pollution (Table 6).

RESULTS OF COD AND BOD5 VALUES TESTED FOAMERS (3% FOREIGN SOLUTIONS)

Table 6

No	Name of foamer	COD [mg.l ⁻¹]	BOD5 [mg.l ⁻¹]	BOD5/COD [%]
1.	Sthamex AFFF 1 %	76.23	22 790	0.33
2.	Sthamex AFFF F-15	73.68	21 370	0.34
3.	Pyronil	79.20	33 530	0.23
4.	Moussol APS F-15	83.46	17 470	0.47

The results of foamer biodegradability suggest that all foamers have little ability to biologically degrade due to the very small proportion of degradable substances.

Acute toxicity

The acute toxicity is the ability or property of foamer to cause severe biological harm or death of the organism in a relatively short exposure time (24 - 96 hours). IC₅₀ was defined as inhibitory concentration of tested substance that causes 50% inhibition of root growth of *Sinapis alba* plants (pure variety of white mustard, seed germination > 90%, seed size 1.5 mm - 2.5 mm) for 72 hours.

The basic monitored parameter for the test evaluation of is the average length of the roots. The value determined in the test solution was compared with control one, and the

percentage of inhibition (reduction) or stimulation (extension of the root) was calculated. The results are listed in Table 7.

RESULTS OF ECOTOXICOLOGICAL TEST FOR SEEDS OF HIGHER PLANTS Table 7

No	Name of foamer	IC _{0,5} *	IC ₁	IC ₂	IC ₃	IC ₅
		%	%	%	%	%
1.	Sthamex AFFF 1 %	96.2				
2.	Sthamex AFFF F-15	87.6	88.3			
3.	Pyronil	98.0				
4.	Moussol APS F-15	66.2	76.7	87.9	89.6	98.3

* Ecotoxicological test on seeds of higher plants *Sinapis alba*, subscript reflects the concentration of sample (volume %). empty box = no sprouted seed.

Ecotoxicological test shows that the higher concentrations are significantly toxic to the tested plant species.

Conclusion

Today, we know many types of fire-fighting foams, which have different physical and extinguishing properties. Each of them has its own pros and cons, as was shown by our testing. It is necessary to know their physical characteristics, e.g. their stability at low and high temperatures defined by half-life, number of foaming specifying whether it is heavy, medium or light foam, and also their viscosity, resistance of fluid to internal friction and other properties to be appropriately selected and used in fire-fighting practice.

Modern fire-fighting foams can be considered as very good in terms of physical characteristics, but, in recent years, the new REACH legislation draws attention to their ecotoxicological properties. If fire-extinguishing foams are used to extinguish large fires, their products (such as decomposed water from the formed foam) are very likely to get into the soil and water flow, while affecting possibly the purification of wastewater. All types of foams have different ecological characteristics, since their components determine the rate of biodegradation. The ecotoxicological tests of *Sinapis alba* also showed that even a low concentration of foamer exhibits significant toxicity.

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This post was created in the framework of grant project **VEGA no. 1/0488/08** entitled **"Environmental impacts of fire-fighting foam for extinguishing fires in nature.**

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