

st. kpt. dr inż. Bernard KRÓL
bryg. dr hab. inż. Andrzej MIZERSKI, prof. SGSP
Zakład Środków Gaśniczych, Szkoła Główna Służby Pożarniczej

Comparison of Properties of Foaming Concentrates Containing Sodium Dodecyl Sulfate (SDS) and Cetyltrimethylammonium Bromide (CTAB) for Rescue and Decontamination Purposes

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The paper presents results of the research of two model and one typical foaming concentrates prepared for rescue operations connected with elimination of chemical and biological contamination. Concentrates include 20% (wt) of surfactants, 25% (wt) of solvent (ethylene glycol monobutyl ether), 2% (wt) of foam stabilizer (1-dodecanol) and 53% (wt) of water. Two surfactants were studied: SDS as the component of the K-1 concentrate and CTAB as the component of the K-2 concentrate. The course of surface tension isotherms, the wetting power and the properties of foams generated by use of the pure foaming solutions and by the same solutions with additions of acids (HCl, H₂SO₄, CH₃COOH), bases (KOH, NaOH, Ca(OH)₂) and oxidants (H₂O₂, ClO₂) were tested.

The K-1 concentrate (with SDS) had twice higher foaming power than the K-2 concentrate (with CTAB). However foam stability measured as the kinetic of solution drainage was much higher in case of foams generated from CTAB based concentrate. In each case foams showed good resistance to acids, bases and oxidants additives. The disadvantage of CTAB based solutions was their low wetting power.

Keywords: wetting, foamability, decontamination.

1. Introduction

Some of the surfactants are used in firefighting and rescue operations. Foaming concentrates are their most usable form. In everyday operations of fire brigades, the foaming agents containing the hydrocarbon surfactants of high surface activity are used the most frequently. They are applied to generate foams used for the suppression of flammable liquid fires and for protection of combustible materials against re-ignition. There are number of different

foaming concentrates, which differ in chemical composition, especially in kind of surfactants being their components.

Except firefighting operations, foaming concentrates can be used for washing off contamination of oil pollutants and dangerous substances released in emergency situations. In the last years, more attention is paid to the possibility of foams application in operations connected with elimination of chemical and biological contamination, especially in decontamination process of tainted objects and areas. Some special foaming preparations have appeared. In some of them there are cationic surfactants [1], which have, besides high surface activity, the bactericidal properties. The firefighting foaming concentrates contain almost only anionic surfactants.

Synthetic high-expansion foam concentrate (S-type) includes 15÷25 wt.% of hydrocarbon surfactants, 20÷30 wt.% of organic solvents, 2÷4 wt.% of stabilizers, some percent of the hydrotropic substances and a small amount of other additives.

2. Experimental

2.1. Materials

For testing purposes, typical synthetic foaming agent (S) and two concentrates, marked as the K-1 and the K-2 were applied. Their composition, based on general composition of the type S foaming agents, was significantly reduced – they contained only the surfactant, the organic solvent, the foam stabilizer and distilled water as follows:

- surfactant (SDS in K-1 and CTAB in K-2) – 20 wt.%,
- diethylene glycol monobutyl ether – 25 wt.%,
- 1-dodecanol (foam stabilizer) – 2 wt.%,
- distilled water – 53 wt.%.

For measurements of foaming power and foam stability, the following solutions in distilled water were used: HCl $c = 0,01\text{M}$ ($\text{pH} \approx 2$), H_2SO_4 $c = 0,005\text{M}$ ($\text{pH} \approx 2$), CH_3COOH $c = 1\text{M}$ ($\text{pH} \approx 2,6$), NaOH $c = 0,01\text{M}$ ($\text{pH} \approx 12$), KOH $c = 0,01\text{M}$ ($\text{pH} \approx 12$), $\text{Ca}(\text{OH})_2$ $c = 0,005\text{M}$ ($\text{pH} \approx 12$). Acid and hydroxide solutions were used for preparation of the K-1 and the K-2 solutions at concentration 2 wt.% and 3 wt.%. As oxidants, the following substances, frequently applied in decontamination operations were used: 30 wt.% solution of hydrogen peroxide [1, 2] and 5 wt.% solution of chlorine dioxide [3, 4]. For preparation of foaming solutions, the concentration of 5 wt.% of hydrogen peroxide and 0,2 wt.% of chlorine dioxide were used. Chlorine dioxide at this concentration has much more bactericidal properties, it is usually applied at concentration 5÷25 mg/dm^3 [1, 5, 6]. The oxidants concentration was 1; 3 and 6 wt.%.

2.2. Methods

2.2.1. Surface tension

The surface tension isotherms of studied concentrates were determined by the ring method (DuNouy method). The tensiometer with the platinum – iridium ring manufactured by the CSC Scientific Company Inc. was used. All solutions were prepared with distilled water at temperature $20 \pm 1^\circ\text{C}$ and ambient temperature $22 \pm 2^\circ\text{C}$. The critical minimal concentration (cmc) and the minimal surface tensions were read off from the isotherms of surface tension.

2.2.2. Wetting power

The wetting power of concentrates was measured by two methods: by measure of the contact angle and by measure of immersion time of the cotton fabric in the solutions. The contact angles on glass and Teflon® surfaces were measured by the Tracker device made by the I.T. Concept company. After putting the drop of solution on the surface, the changes of contact angle were registered for 30 to 100 s. The concentrates solutions in distilled water at the concentration 1, 5 and 10 g/dm^3 were used.

The method of determination of immersion time of hydrophobic cotton fabric is used for the comparative tests of the wetting agents. There is a special, standard version of this method for textile industry [10]. In the described tests the fabric rings of 20 mm diameter were used. They were fastened to the frame by the thread, drown in examined solution and then the immersion time was measured.

Tests were carried out for the solutions at different concentrations and the figures of immersion time as a function of solution concentration were prepared. As a comparative criteria, there was applied a concentration at which the immersion time was 15 s. (these criteria were accepted by the authors in comparative tests of wetting power of foaming agents and special wetting agents).

2.2.3. Foamability

Foams made of examined concentrates (solutions) were produced by use of laboratory foam generator presented on fig. 1.

The air running through the device is divided into two streams, from which one is flowing into the vessel with foaming solution and produces positive pressure, which causes the flow of the solution through the spray nozzle. The second air stream is flowing through the pipe and mixes with the solution sprayed by the nozzle in the mixing chamber. In some part of the chamber there are steel nets, which provoke the additional turbulence of the foam stream. Thanks to that, the average bubbles' size decreases and the foam becomes more homogenous. This structure of foam means its good stability. The generated foams are similar to the dry foams produced by the Compressed Air Foam System, what's more they have better stability and expansion ratio.

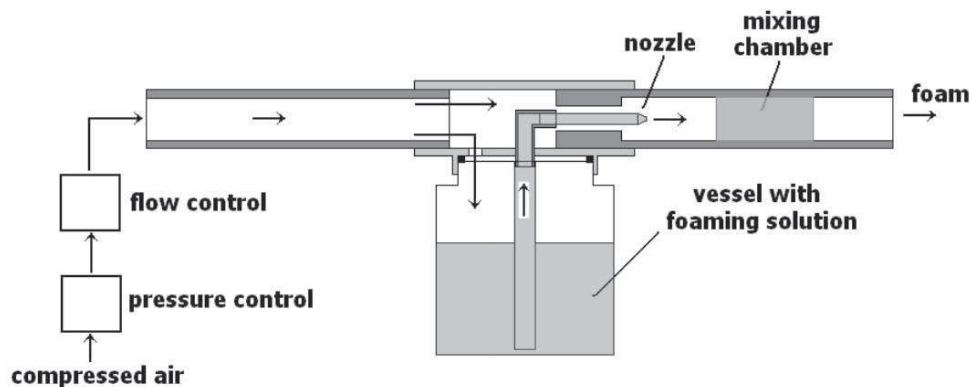


Fig. 1. Foam generator [6]

The foams generation was started 10 minutes after the solution had been prepared. The expansion ratio and the time to drainage of 50% of the foam solution were measured. After the generation, the foam was collected in the vessel of 1200 cm³ of volume and the expansion ratio was calculated, as the proportion of the vessel volume [cm³] to the foam weight [g]. The solution drainage time was measured on the standard stand according to the PN-EN 1568 [11]. The volume of the foam was equal to 1560 cm³. The measurement was carried out until 50% of the initial volume of the solution leaked from the foam sample. The initial volume of the solution was calculated as the proportion of foam volume [cm³] to the expansion ratio. For each sample, the figure of the drainage time was drawn and characteristic parameters W_5 and $W_{0.5}$ were read off. The W_5 is the percent of foam solution, which drainages during the first 5 minutes after foam was prepared, the $W_{0.5}$ is the time to drainage of 50% of the foam solution collected in foam structure. Foams were prepared from the model concentrates in tap water at the concentration of 1, 2, 3 and 6 wt.%. The solutions temperature was $20 \pm 1^\circ\text{C}$, and the ambient temperature was $22 \pm 2^\circ\text{C}$.

The same foam generator was used for testing the influence of acids, bases and oxidants, at concentrations of 2 and 3 wt.%, on foams properties.

3. Results and discussion

3.1. Surface tension

Minimal surface tensions of foaming solutions are much lower than those of pure surfactants (fig. 2). In case of the SDS solution the difference was ca. 15 mN/m, similar to earlier work [7] and in case of CTAB the difference was about 10 mN/m. The critical micelle concentration read off from the figure for K-1 concentrate was 3.5 mmole/dm³ in comparison to 8.2 mmole/dm³ for pure SDS [8, 9]. Then, the cmc for the K-2 concentrate (1,4 mM) was higher than the values obtained for the CTAB solutions without any additions (0.92 mmole/dm³) [5].

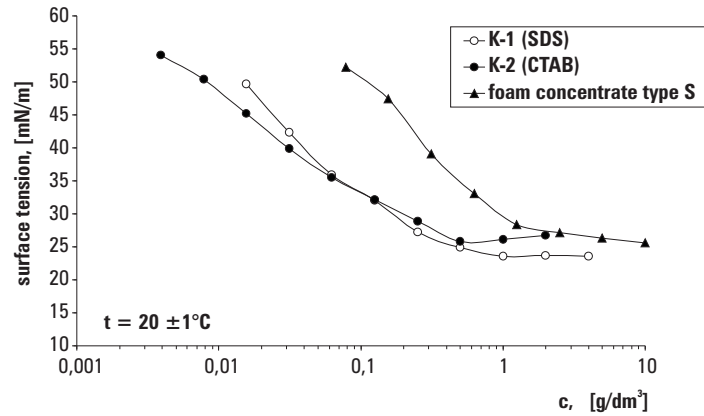


Fig. 2. The isotherms of surface tension of measured concentrates

3.2. Wetting power

3.2.1. Contact angle

Changes of foaming solutions contact angles as a function of time determined on PTFE and glass surfaces were presented on figures 3 and 4.

Figures 3 and 4 show that the K-2 concentrate has worse wetting power than the K-1. Different dependence was visible in the first stage of the PTFE surfaces wetting by the solutions at concentration of 1 and 5 g/dm³. In the case of glass surfaces wetting by the solutions at the same concentration, the contact angles for the K-2 concentrate were lower in the first stage than in case of the K-1.

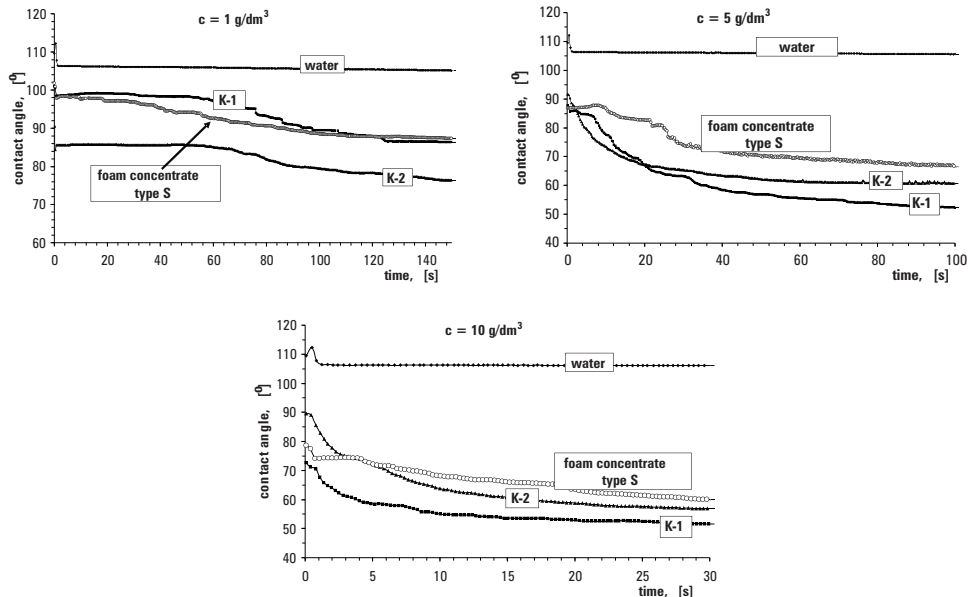


Fig. 3. Changes of foaming solutions contact angles as the function of time (PTFE surface)

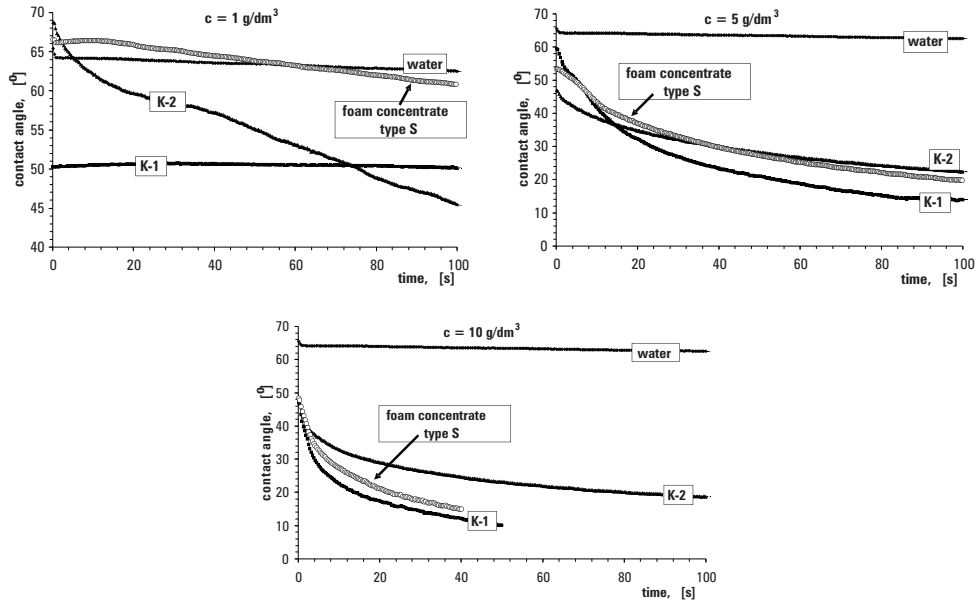


Fig. 4. Changes of foaming solutions contact angles as the function of time (glass surface)

The immersion time of the K-2 at concentration of 1 g/dm^3 was 70 s (fig. 6). This concentration was higher than the cmc for the K-2 and similar to the cmc for the K-1, which explains better wetting power of K-2 concentrate. However, it doesn't testify better wettability of SDS in comparison to CTAB.

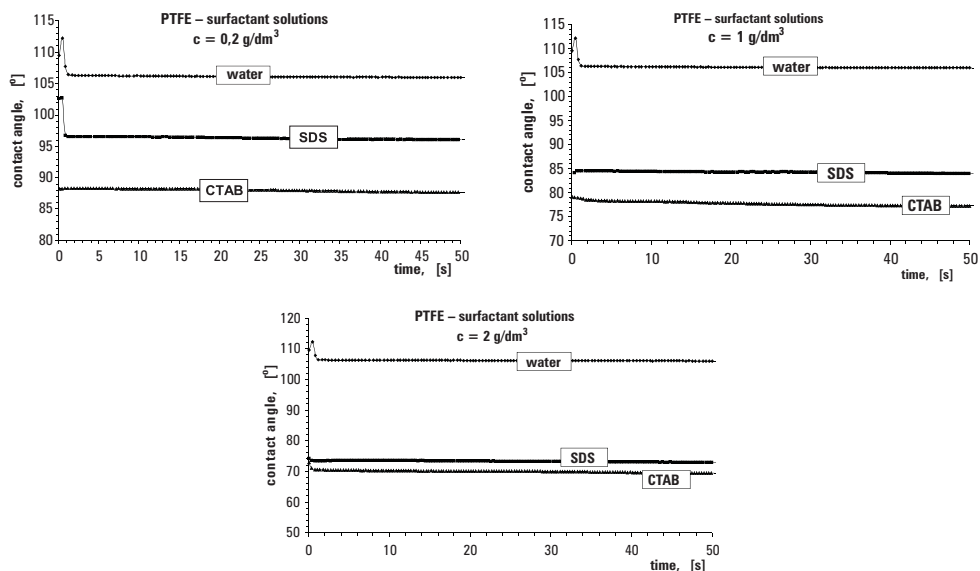


Fig. 5. Changes of surfactants solutions contact angles as the function of time (PTFE surface)

Some tests of the PTFE surfaces wetting by pure surfactants, at concentration suited to their concentration in normal foaming concentrates were carried out (fig. 5). In each case the contact angles for the CTAB solutions were lower than for the SDS solutions. The equilibrium state was achieved quickly and the contact angles changed slightly.

3.2.2. Immersion

In the wetting power test by the immersion of cotton fabric, the K-1 concentrate had better properties (fig. 6). This method was earlier used for the determination of surfactants usability as wetting agents for firefighting purposes. The wetting power was defined as the solution concentration, at which the immersion time of cotton

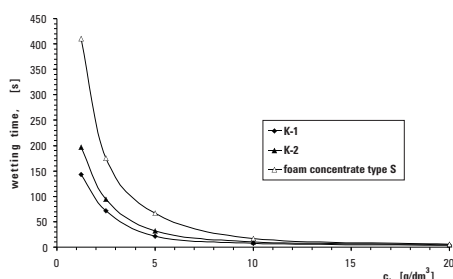


Fig. 6. The wetting time of hydrophobic cotton fabric as a function of surfactant concentration

disc was equal to 15 s. The concentrate has to have wetting power at least 20 g/dm^3 to be accepted as a good wetting agent. On figure 6 the wetting curve for the standard type S foaming agent was shown. The wetting power of the K-1 and the type S foaming agent was equal to 6 g/dm^3 and of the K-2 to $7,8 \text{ g/dm}^3$. At lower solutions concentrations, the immersion times of the cotton disc in the K-2 solutions were lower than in the foaming agent solutions.

3.3. Foamability

The method of foam generation, which we have used, allows to differ the foaming properties of concentrates better, than the methods which use the standard devices. The tests showed that the K-1 concentrate had much better foaming power than the K-2. However, the foams generated from the K-2 solutions had considerably higher stability, except concentration of 1% when the K-2 foam had very low expansion ratio (fig. 7). Such high foam stability is not necessary in case of extinguishing operation, especially when suppressing inflammable liquid fires, because it is connected with decreased spreading

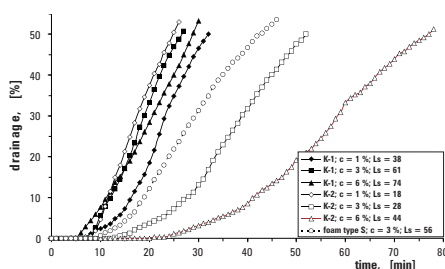


Fig. 7. The curve of drainage as the function of time (L_s – foam expansion ratio)

ability. This capability can be useful when the foam is applied in the decontamination operations, when it is necessary to keep foam on contaminated surfaces for a long time. The foaming powers of the K-1 concentration are similar to those of the type S foaming agents. Foams, at concentration equal to 3% had similar expansion ratios, but their stability was significantly higher. It results from the

fact, that the quantitative ratio of surfactant to stabilizer in the K-1 concentrate is optimal.

3.3.1. Influence of acids and hydroxides additions on foams properties

Foams properties with additions of acids and bases are presented in table 1. For comparative purposes, the characteristics of the type S foaming agent are also shown.

Table 1. Properties of foams with addition of acids and bases
pH (H₂SO₄, HCl) ≈ 2; pH (CH₃COOH) ≈ 2,6; pH [NaOH, KOH, Ca(OH)₂] ≈ 12
E – foam expansion ratio

Concentrate	c [wt.%]	Medium or additive	E	W ₅ [%]	W _{0,5} [min]	Medium or additive	E	W ₅ [%]	W _{0,5} [min]
Foam concentrate type S	2	water	44,3	0	39,0	water	44,3	0	39,0
		CH ₃ COOH	35,0	0	34,5	NaOH	44,7	0	36,7
		HCl	34,2	0	31,0	KOH	41,7	0	37,5
		H ₂ SO ₄	39,0	0	34,5	Ca(OH) ₂	25,8	0	54,5
	3	water	56,1	0	42,5	water	56,1	0	42,8
		CH ₃ COOH	47,8	0	42,5	NaOH	47,0	0	53,3
		HCl	51,5	0	36,5	KOH	50,5	0	53,7
		H ₂ SO ₄	52,0	0	39,0	Ca(OH) ₂	33,2	0	65,5
K-1	2	water	55,2	7,1	15,6	water	51,7	7,9	16,3
		CH ₃ COOH	57,2	8,1	11,9	NaOH	53,1	10,2	18,5
		HCl	60,7	10,5	14,2	KOH	54,7	0	32,5
		H ₂ SO ₄	60,6	10,0	14,9	Ca(OH) ₂	11,4	6,6	57,7
	3	water	72,1	0	29,0	water	71,0	7,2	17,9
		CH ₃ COOH	65,4	10,1	14,2	NaOH	70,2	3,8	21,2
		HCl	75,0	0	31,7	KOH	68,5	11,4	14,1
		H ₂ SO ₄	71,5	0	26,0	Ca(OH) ₂	57,7	16,2	15,9
K-2	2	water	31,7	0	34,0	water	35,1	0	45,5
		CH ₃ COOH	27,3	0	25,5	NaOH	30,0	0	48,8
		HCl	35,8	0	36,0	KOH	37,8	0	41,0
		H ₂ SO ₄	33,6	0	31,0	Ca(OH) ₂	37,9	0	41,5
	3	water	37,0	0	51,0	water	37,4	0	61,8
		CH ₃ COOH	36,5	0	39,0	NaOH	40,0	0	43,0
		HCl	34,0	0	57,0	KOH	40,0	0	54,3
		H ₂ SO ₄	36,7	0	47,5	Ca(OH) ₂	39,0	0	72,0

The influence of acid addition on the properties of the K-1 foams was significant. At the concentration of 2 wt.% we noticed the increase of expansion ratios in comparison to foams without any additions. The similar situation was observed in the case of solutions at concentration of 3 wt.%, except those with addition of acetic acid, where the expansion ratio was 10% lower. Additions of acids decreased the foam stability, especially in case of acetic acid, which worsened it the most, at each concentration. The sulfuric acid had the weakest influence on the properties of foams generated by the use of the K-1 concentrate.

Additions of the sulfuric acid and the hydrochloric acid didn't change the properties of the K-2 concentrate foams. The decrease of foaming power in the acetic acid solutions were visible only at concentration of 2 wt.% and even if the diminution of foam stability was significant, the foam could be accepted as considerable stable. Addition of the hydrochloric acid had the least influence on foams produced by the use of the K-2 concentrate.

Foams generated by the use of the type S foaming agent were very stable. The addition of acids decreased the foam expansion ratio by about 20% for 2 wt.% solutions and to 10 ÷ 15% for 3 wt.% solutions.

Foams produced from 2 wt.% solutions with acids addition had lower stability than those without any addition, but the stability was still high. For 3 wt.% solutions only, the foam with hydrochloric acid had lower stability. Sulfuric acid had the lowest influence on the foams properties.

The K-1 solutions reacted to bases (hydroxides) addition in different manner. The biggest decrease of the expansion ratio was observed for the 2 wt.% solution with calcium hydroxide. Its value was equal to 11,4, while for foam without any addition – 51,7. However this foam had much higher stability. $W_{0.5}$ value was 57,7 min. – three times higher than the foam without any supplement. Potassium hydroxide addition to 2 wt.% solution increased the expansion ratio and the stability, but at concentration equal to 3 wt.% and at similar expansion ratio, the foam was less stable. Only addition of sodium hydroxide influenced positively the foams properties at each concentration.

Hydroxides addition affected slightly the foaming power of the K-2 solutions. The stability of foam with additions of the calcium hydroxide generated from 2 wt.% solution, didn't change much, whereas it increased significantly in the case of 3 wt.% solutions. At this concentration, only the addition of sodium hydroxide decreased the foam stability and didn't change the expansion ratio.

In the case of the type S foaming solutions, it was also the calcium hydroxide, that had the biggest negative influence on foaming power. Foams produced from 3 wt.% solution with the sodium hydroxide had lower expansion ratio too. Generally, the stability of foam with the hydroxides addition was higher or didn't change. The highest increase of the foam stability was observed for foams with the addition of calcium hydroxide.

3.3.2. Influence of oxidants addition on foams properties

The properties of foams with addition of hydrogen peroxide and chlorine peroxide are compared in table 2.

Table 2. Properties of foams with oxidants addition

c [wt.%]	additive	K-1			K-2		
		E	W ₅ [%]	W ₀₅ [min]	E	W ₅ [%]	W ₀₅ [min]
1	none	38	0	31,6	18	0,1	25,0
	5 wt.% H ₂ O ₂	31	1,2	23,5	25	0	30,1
	0,2 wt.% ClO ₂	43	7,7	16,3	24	0,2	27,5
3	none	61	0	26,8	28	0	52,0
	5 wt.% H ₂ O ₂	67	0	33,8	34	0	64,0
	0,2 wt.% ClO ₂	75	0	28,0	29	0	34,8
6	none	85	0	47,0	44	0	76,9
	5 wt.% H ₂ O ₂	80	0	28,4	36	0	>100
	0,2 wt.% ClO ₂	71	0	32,7	21	0	58

Oxidants have generally negative influence on foaming power and the properties of foams generated from the K-1 solutions. Only at 3 wt.% concentration, foams have better properties than those without any additions. The K-2 concentrate is less sensitive to oxidant addition. Foams with the hydrogen peroxide have higher expansion ratio and stability, than those without any supplement. Foams with the chlorine dioxide generated from the foaming solutions at 3 and 6 wt.% concentration had lower stability, but acceptable for rescue purposes. However in the chlorine dioxide solution at concentration equal to 6 wt.%, 50% the fall of expansion ratio was found.

4. Conclusions

- The K-1 concentrate has the composition similar to that of the extinguishing standard type S foaming agents. The expansion ratios of generated foams were even higher than in the case of typical foaming agents, but their stability is lower. Acids, bases (hydroxides) and oxidants addition influence in some degree foams properties, but this negative effect can be reduced by higher solution concentration. Consequently, the standard foaming agents with the anionic surfactants should behave in a similar manner.

- The K-2 concentrate has indeed worse foaming power than the K-1, but generated foams have high stability. The lower foam efficiency can be compensated by longer holding of foam on vertical surfaces, which is important in the case of operations concerning decontamination process. Probably, the quaternary cationic surfactants, with long alkyl radicals have the ability of creating

stable foams. The Sandia Decontamination Foam [1] contains those surfactants, and foams produced from this solution have a very high stability.

- Foaming preparations based on cationic surfactants can be applied to generate decontamination foams, thanks to high foam stability and bactericidal properties. However they can have, in comparison to anionic surfactants, significantly worse wetting power. Though CTAB had better wettability to the PTFE than SDS, but in the case of the K-1 and the K-2 concentrates it is opposite. When wetting the hydrophobic fabric, the K-1 concentrate was also better. The problem of the cationic surfactants concentrates wettability needs more research, because the highly dispersed, stable foams, generated from the solutions of weak wetting ability don't stick to vertical surfaces. The similar situations are observed in the case of small-bubbled, stable foams, produced from foaming agents containing protein hydrolyzates. They have very poor wetting power and highly dispersed foams don't stick to vertical surfaces and ceilings.

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Bernard KRÓL
Andrzej MIZERSKI

Porównanie właściwości koncentratów pianotwórczych zawierających dodecylosiarczan sodu (SDS) i bromek cetylotrimetyloamonionowy (CTAB) stosowanych do celów ratowniczych i dekontaminacji

W artykule przedstawiono wyniki badań dwóch modelowych (K-1, K-2) oraz jednego typowego handlowego preparatu pianotwórczego (S). Są one przeznaczone do działań związanych z usuwaniem zagrożeń chemicznych i biologicznych. Badano wpływ dodatków kwasów, zasad oraz utleniaczy na właściwości roztworów środków pianotwórczych (zdolność zwilżania, zdolność pianotwórcza, trwałość pian).

STRESZCZENIE