



New water-based fire extinguishant: Elaboration, bench-scale tests, and flame extinguishment efficiency determination by cupric chloride aqueous solutions



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ABSTRACT

A new aqueous fire-extinguishing agent (AFEA) – the 40% aqueous solution of CuCl_2 – was elaborated. The AFEA was prepared by dissolving copper(II) chloride dihydrate in water. The resulting solution was characterized by a series of physicochemical methods. The ability of the CuCl_2 -containing AFEA to suppress the hydrocarbon flame has been investigated under conditions of an enclosed space according to the all-Union State Standard 3789 and open space by means of elaborated technique. The testing results have revealed a short-term exposure of the 40% aqueous solution of CuCl_2 directly onto flame causes the efficient inhibition of fire. It has been ascertained that under conditions of the experiment, the extinguishment duration of the seat of fire (the special fire of B_1 class) by the CuCl_2 -containing AFEA aerosol was 0.6 s; this is 26 times more efficient than the same extinguishment by water aerosol. The experimental ascertained values of the AFEA aerosol feed intensity (I_{AFEA}) and the minimal expenses of the AFEA to extinguish the seat of fire of B_1 class are $0.057 \text{ L}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ and $0.034 \text{ L}\cdot\text{m}^{-2}$, respectively. These data have become a reliable basis to explain the hydrocarbon flame suppression mechanism by aqueous solutions of copper(II) salts.

1. Introduction

A systematic search for new chemicals that could suppress efficiently flame propagation and demonstrate high fire-extinguishment performance is an important fire safety problem that must be solved immediately. To date, water is the most common substance to extinguish fires. The ordinary water owing to unique physical properties, such as the high molar heat capacity ($c_{\text{M}}(\text{H}_2\text{O}) = 75.9 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) and the vaporization enthalpy ($\Delta H_{\text{vap}}^{\circ}(\text{H}_2\text{O}) = 41.42 \text{ kJ}\cdot\text{mol}^{-1}$), can very efficiently suppress a flame because of its extraordinary ability to cool, insulate, and dilute. But, the cooling effect of water can be improved greatly by using finely dispersed water [1]. The water-spray use also reduces the application flux of water [2]. Certainly, the cooling efficiency of gaseous products of combustion is determined as well by the aerosol feed intensity. The considerable cooling effect of the finely dispersed water is caused by increase of the heat-transfer coefficient and decrease of the heating time of water droplets because at this case the total surface area of water-droplets is enlarged substantially [3]. But water, as fire-extinguishing agent, reveals a kind of chemical inertness with respect to most substances and materials, that is, water is not able

to affect the flame chemically. That is why water never effects the flame chemically during the extinguishment of fires [4]. On the contrary, water in many cases can be an accelerant of burning. Boiling petroleum products are able to ignite spontaneously after contacting water!

In the world practice of recent times, new fire-extinguishing technologies have been introduced. Among them, the spray technology of the aqueous solutions of various inorganic salts takes up a special position. It is important to note that aqueous solutions of inorganic salts are able to provide efficient suppression of flame by combining the unique physical and chemical properties of water and inhibitory function of dissolved salts [5]. In this case, the inhibitors of combustion are the alkali and alkaline earth metals salts, as well as ammonium salts. These salts are substances mostly that dissolve readily in water, and these have to be used in the form of concentrated solutions to suppress the flame efficiently [6]. There was well studied previously the ability of some inorganic potassium salts to extinguish the fire. These studies have become the found to make the AFEAs based on K_2CO_3 [7] and KNO_3 [8] to extinguish fires of "A" and "B" classes.

To increase the effectiveness of fire extinguishing, another AFEA was proposed in Ref. [9]. The preparation of such a composite is based

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on the chemical reactions of the acetic acid and the citric acid with the alkali (KOH) with the addition of certain inorganic salts (K_2CO_3 , $KHCO_3$, $K_4P_2O_7$, $NaHCO_3$ etc.) to stabilize the reaction. Other AFEAs are produced from waste of titanium manufacture, that is, from the melts of the *s*-metals chlorides (KCl, NaCl, $MgCl_2$) with the addition of a little amount of *d*-metals chlorides ($MnCl_2$, $CrCl_3$, $FeCl_3$) [10].

There were published recently articles [11–18] relating to the elaboration of new AFEAs based on the transition metals salts. The high fire-extinguishing efficiency of aqueous solutions of such salts is due to the specific ability of *d*-atoms to accept electrons that frequently results in the formation of coordination compounds. Undoubtedly, this feature of the transition metal salts provides AFEAs with the necessary properties to bond the radicals of the flame and to interrupt the chain reactions. In order to prepare these AFEAs, researchers used such salts of *d*-metals as $CoCl_2$, $NiCl_2$, $MnCl_2$, $FeCl_2$ et al. However, among many well-known water-soluble *d*-metal compounds (inhibitors of burning), the complexes of potassium with iron [19] deserve special attention. In particular, concentrated aqueous solutions of potassium hexacyanoferrate(II) ($K_4[Fe(CN)_6]$) and, especially, potassium hexacyanoferrate(III) ($K_3[Fe(CN)_6]$) show high fire-extinguishing efficiency [20]. The tests of the water-based fire-extinguishing agent have revealed that extinguishment of forest fires by the 30% aqueous solution of $K_3[Fe(CN)_6]$ suppresses very efficiently both a flame and a smoldering. Here, besides heat-absorbing properties, the exceptional ability of iron(III) complex salts aqueous solutions to suppress the flame effectively is also due to the chemical affinity of electron-acceptor atoms of Fe(III) to the electron-donor atoms of O, N, S existing in the flame in the form of chemical radicals. In general, the interaction of water-soluble salts of *d*-metals with the active chemical radicals in the fire is considered to be the most likely mechanism of the flame suppression. Unfortunately, the use of $K_3[Fe(CN)_6]$ as an inhibitor of combustion has one significant disadvantage. First of all, it is about formation of highly toxic products of thermal decomposition of this salt. In view of this, such a *d*-metal salt as copper(II) chloride is considered a very promising inorganic substance to elaborate a new AFEA [21]. Just as a majority of transition metals, Cu atoms of copper(II) chloride also discover exceptional chemical affinity to heteroatoms and active particles of flame – chemical radicals. But copper(II) chloride, unlike potassium hexacyanoferrate(III), is thermally more stable and can easily be converted into a gaseous phase at high temperatures. Such a thermal behavior of $CuCl_2$ is the key to understand the processes occurring in the flame during its extinguishing.

Taking into account the above, we were able to elaborate a new AFEA based on water-soluble copper(II) chloride and to study the fire-extinguishing properties of the $CuCl_2$ aqueous solution aerosol. The article presents the results of synthesis and fire-extinguishing tests of the elaborated AFEA, using, at that, the seat of fire of B class. Since the copper(II) chloride has noticeable fire-extinguishing properties, the particular attention will be paid to the hydrocarbon flame suppression mechanism by aerosols of the $CuCl_2$ aqueous solutions.

2. Experimental

2.1. Materials

To prepare water-based fire extinguishant and study its fire extinguishing properties, the following chemicals were used: an inhibitor of burning (base of AFEA) – the copper(II) chloride dihydrate

($CuCl_2 \cdot 2H_2O$) [22] (blue-green crystals, $M_r = 170.48$, $\rho = 2.51 \text{ g}\cdot\text{cm}^{-3}$, solubility in water ($\text{g}/100 \text{ g H}_2\text{O}$) – 70.6, 75.7 and 107.9 at 0 °C, 25 °C and 100 °C, respectively); a foaming agent (FA) (addition to AFEA) – the ammonium *n*-alkylsulfate ($[C_nH_{2n+1}SO_3^-]NH_4^+$, where $n = 12\text{--}16$) ($M_r = 267\text{--}323$ ($\bar{M}_r = 295$), $\rho = 1.020(1) \text{ g}\cdot\text{cm}^{-3}$, $\sigma = 30.36(1) \text{ mN}\cdot\text{m}^{-1}$, $\eta = 7.068(4) \text{ mm}^2\cdot\text{s}^{-1}$ pH = 8.6); a fire source (nonpolar (seat of fire of B₁ class) and polar (seat of fire of B₂ class) hydrocarbons) – “B₁”: *n*-hexane (C_6H_{14}) ($M_r = 86$, $\rho = 0.660(1) \text{ g}\cdot\text{cm}^{-3}$, $T_{\text{melting}} = -95.3 \text{ }^\circ\text{C}$, $T_{\text{boiling}} = 68.7 \text{ }^\circ\text{C}$, $T_{\text{flash}} = -20 \text{ }^\circ\text{C}$, $T_{\text{flame}} = 835 \text{ }^\circ\text{C}$, $r_{\text{regression}} = 25\text{--}30 \text{ cm}\cdot\text{h}^{-1}$) or diesel fuel ($M_r = 204$, $\rho = 0.824(1) \text{ g}\cdot\text{cm}^{-3}$, $T_{\text{boiling}} = 246 \text{ }^\circ\text{C}$, $T_{\text{flash}} = 65 \text{ }^\circ\text{C}$, $T_{\text{self-ignition}} = 210 \text{ }^\circ\text{C}$, $T_{\text{flame}} = 1100 \text{ }^\circ\text{C}$, $r_{\text{regression}} = 18\text{--}20 \text{ cm}\cdot\text{h}^{-1}$), “B₂”: monoethanolamine ($HOC_2H_4NH_2$) ($M_r = 61$, $\rho = 1.012(1) \text{ g}\cdot\text{cm}^{-3}$, $T_{\text{melting}} = 10.3 \text{ }^\circ\text{C}$, $T_{\text{boiling}} = 171 \text{ }^\circ\text{C}$, $T_{\text{flash}} = 90 \text{ }^\circ\text{C}$, $T_{\text{ignition}} = 108 \text{ }^\circ\text{C}$, $T_{\text{flame}} = 815 \text{ }^\circ\text{C}$) [23]. All reagents have been purchased through commercial sources and used as-received without further purification.

2.2. Preparation and characterization of the $CuCl_2$ -containing AFEA

The $CuCl_2$ -containing AFEA was prepared by dissolving of copper (II) chloride in water. The crystalline $CuCl_2 \cdot 2H_2O$ (1030 g, 6 mol) was added to 1000 cm^3 of water, next the mixture was heated to temperature of 70–80 °C till full dissolving the salt. The resulting solution must be necessarily acidified with concentrated HCl (2 cm^3) to avoid hydrolysis of $CuCl_2$ and subsequent precipitation of $Cu(OH)_2$. The emerald $CuCl_2$ aqueous solution was cooled to room temperature and then the FA (1.5 cm^3) was added to enhance the AFEA spray properties. The droplets-size distribution function of aqueous aerosol versus an amount of the added FA has been defined in Ref. [24]. The measurements have shown that without a FA the average diameter of droplets of aqueous aerosol is about 400 μm , while after addition of the FA this value is about 300 μm .

The prepared $CuCl_2$ -containing aqueous solutions were characterized by a series of physicochemical methods. The kinematic viscosity (η) has been measured by the viscosimetry method (the VLA–1 viscometer, the capillary inner diameter is 0.99 mm). The surface tension (σ) has been determined by the method of droplets amount counting using the ST–1 stalagmometer. The specific density (ρ) has been ascertained by the bottle method; the acidity (pH) has been measured using the 150MI pH-meter. The freezing point of the solutions has been calculated according to the Raoult's law. The physicochemical properties of the $CuCl_2$ -containing aqueous solutions are given in Table 1.

2.3. Fire extinguishing tests of the $CuCl_2$ -containing AFEA

2.3.1. Testing in an enclosed space

The fire-extinguishing efficiency of the $CuCl_2$ -containing AFEA have been determined according to the all-Union State Standard 3789 [25] using the equipment displayed in Fig. 1. It is made up of the test chamber in the parallelepiped shape (outer size is 0.7 m × 0.6 m × 0.45 m; the net volume is 0.19 m^3) in which is put a seat of fire of B class. The top of the chamber has an orifice ($\varnothing = 10 \text{ cm}$) connecting to a chimney. The equipment also comprises a graduated cylinder for determination of the AFEA expense, a device for the AFEA feed (the certificated Carbon Dioxide Fire-Extinguisher (CDFE-5) possessing the volume of 5 dm^3 and sprinkler ($\varnothing = 1.0 \text{ mm}$)) and a stopwatch (precision class is $\pm 0.2 \text{ s}$).

To generate fire source whose parameters have meet petroleum

Table 1

The physicochemical properties of the $CuCl_2$ -containing aqueous solutions.

Aqueous solution	ρ ($\text{g}\cdot\text{cm}^{-3}$)	η ($\text{mm}^2\cdot\text{s}^{-1}$)	σ ($\text{mN}\cdot\text{m}^{-1}$)	pH	T_{freezing} ($^\circ\text{C}$)
40% $CuCl_2$	1.400(1)	2.987(3)	88.71(1)	1.07	–33.5
40% $CuCl_2$ + 1% FA	1.400(1)	3.047(3)	31.93(1)	1.1	–33.5

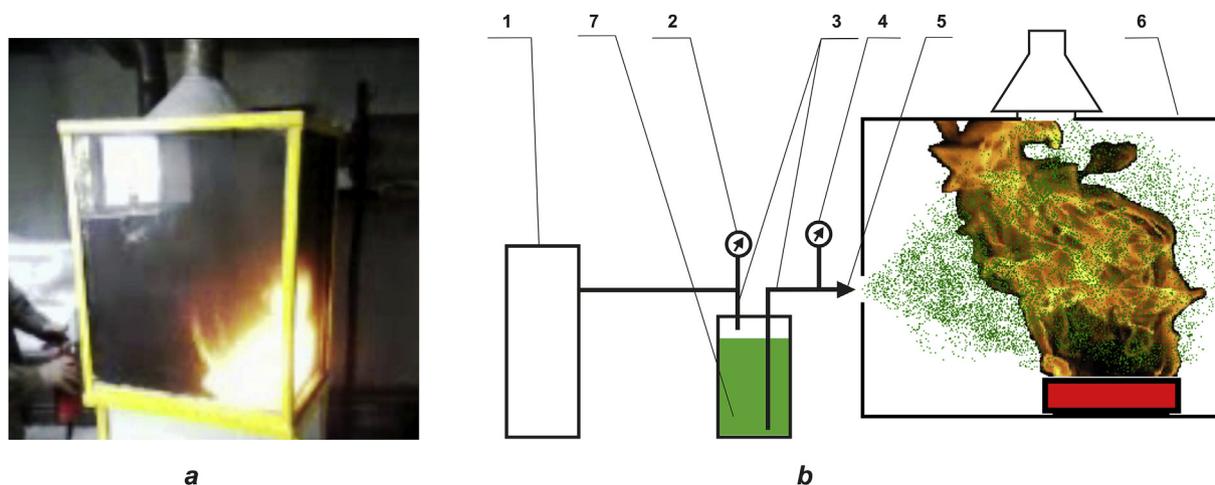


Fig. 1. General view of the test chamber designed to determine the fire-extinguishing performance in an enclosed space (a) and its schematic image (b): 1 – compressed air cylinder; 2, 4 – pressure gauges; 3 – connecting hoses; 5 – nozzle of sprinkler; 6 – test chamber with fire source in the inside; 7 – device for the AFEA feed.

products combustion, the seat of fire of B class was made. It is a round pan of steel (lip thickness, height, and diameter are 0.001 m, 0.05 m, and 0.18 m, respectively; the net volume is 1250 cm³) filled with inflammable liquid (*n*-hexane or monoethanolamine) and placed on the bottom of the test chamber. *n*-Hexane (800 cm³) or monoethanolamine (800 cm³) that simulates the seat of class B₁ or B₂, respectively was poured into the pan (ullage 30 mm).

The fire extinguisher of CDFE-5 type was filled by the CuCl₂-containing AFEA prepared in advance (see technique described in section 2.2) and then an excess pressure (6 atm) was produced inside its case using the compressed air cylinder (Fig. 1, b). The AFEA aerosol was atomized by means of a screw cone sprinkler. It was ascertained experimentally the supply productiveness (*Q*) of the CuCl₂-containing AFEA was 0.0045(2) L·s⁻¹ (for comparison, *Q*_{water} = 0.0054(2) L·s⁻¹).

The pan with fuel, previously placed in the test chamber, is set fire to. The free burning of fuel lasted 60 ± 5 s provided that the test chamber door was lifted by 5 cm. AFEA was injected directly into the flame through a hole in the side wall using a fire extinguisher. The flame extinguishment duration ($\Delta\tau_{\text{exting.}}$) was defined as the interval of time from the injection moment to the moment of complete cessation of burning.

The fire-extinguishing efficiency of the AFEA was determined separately for the hexane flame and the monoethanolamine flame. Besides, the AFEA tests were carried through for the 40%, 20%, 10%, and 5% aqueous solution of CuCl₂ and for the tap water. The increase factor of the fire-extinguishing efficiency (*K*₁) of the AFEA as to water was calculated using the following relationship:

$$K_1 = \frac{V_{\text{water}}}{V_{\text{AFEA}}}, \quad (1)$$

where *V*_{water} or *V*_{AFEA} is corresponding volume of water or AFEA expended on the flame extinguishment.

The tests of fire extinguishing efficiency of each AFEA type were accompanied, at least, by 3–5 measurements. The averaged results as to extinguishment of flame in an enclosed space using the CuCl₂-containing solutions are presented in Table 2.

2.3.2. Testing in an open space

Fire extinguishing experiments with the CuCl₂-containing solutions (AFEAs) in an open space were carried out in accordance with the elaborated technique described in Ref. [26] on the installation shown in Fig. 2. It is made up of the pneumatic sprayer (Record 2200 ESO) with a built-in container (500 cm³) and the nozzle of the sprinkler (∅ 1.2 mm), the compressed air cylinder equipped with the reducing gear

Table 2

The testing results of the CuCl₂-containing AFEA in an enclosed space.

AFEA	Seat of fire of B ₁ class (<i>n</i> -hexane)			Seat of fire of B ₂ class (monoethanolamine)		
	<i>V</i> _{AFEA} (L)	$\Delta\tau_{\text{exting.}}$ (s)	<i>K</i> ₁	<i>V</i> _{AFEA} (L)	$\Delta\tau_{\text{exting.}}$ (s)	<i>K</i> ₁
40% CuCl ₂	0.0067(2)	1.5(2)	6.9	0.0035(2)	0.8(2)	11.3
20% CuCl ₂	0.0117(2)	2.5(2)	3.9	0.0053(2)	1.2(2)	7.4
10% CuCl ₂	0.0185(2)	4.0(2)	2.5	0.0109(2)	2.8(2)	3.6
5% CuCl ₂	0.0325(2)	6.5(2)	1.4	0.0226(2)	4.8(2)	1.7
0% CuCl ₂ (tap water)	0.0461(2)	9.0(2)	1	0.0395(2)	7.5(2)	1

to regulate pressure at the system (about 6–8 atm) and pressure gauges with a maximum measuring limit of 1.6 MPa, as well as a round, cast-iron pan (lip thickness, height, and diameter are 0.003 m, 0.08 m, and 0.3 m, respectively; the net volume is 5500 cm³). The combustible liquid (diesel fuel or A-76 (A-80) gasoline) met all-Union State Standard 4063 [27].

The pan is filled first with tap water (2000 cm³) and then with a non-polar hydrocarbon (1000 cm³); a volume ratio of water to fuel is 2:1 (ullage is 50 mm). The prepared fuel is set fire to. After 60 s of free combustion, the AFEA is sprayed over the burning fuel. All experiments were carried out in an open space where the speed of the air flow near the fire did not exceed 0.5 m·s⁻¹, and the air temperature varied from 15 to 20 °C. In accordance with the size of the pan (*S* = 0.071 m²) it was necessary to set a nozzle of the pneumatic atomizer so that the aerosol completely enveloped the whole surface of the pan. The specified parameters of the installation, be able to ensure reproducibility of the results, had the following characteristics: *L* = 110 cm, α = 30°, $\varnothing_{\text{sprayer-hole}}$ = 1.2 mm, *P*_{jet} = 6 atm, *Q* is 0.0040 L·s⁻¹ and 0.0070(2) L·s⁻¹ for AFEA and water, respectively (see Fig. 2).

Fire extinguishing tests of the AFEA in an open space were carried out for a 40% aqueous solution of the CuCl₂ with and without FA addition, as well as for tap water with and without FA addition. Each test was triply repeated. The result was considered positive if flame extinguishment duration did not exceed 30 s. The averaged results for above experiments are given in Table 3.

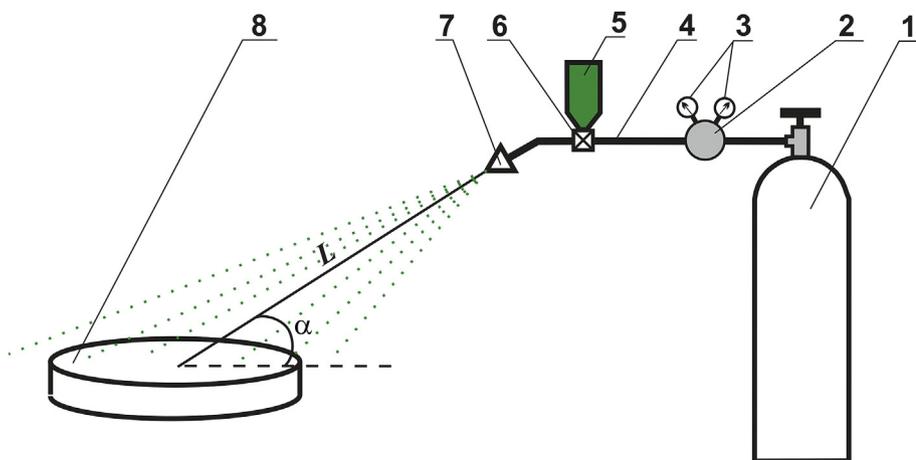


Fig. 2. The scheme of the installation for the fire-extinguishing tests in an open space: 1 – compressed air cylinder; 2 – reducing gear; 3 – pressure gauges; 4 – connecting hose; 5 – container for AFEA feed; 6 – release gear of the pneumatic sprayer; 7 – nozzle of sprayer; 8 – pan with combustible liquid (seat of fire of B₁ class).

Table 3
The averaged results of fire extinguishing tests of the CuCl₂-containing AFEA in an open space.

AFEA	V _{AFEA} (L)	Δτ _{exting.} (s)	K ₁
Tap water	0.0627(2)	9.0(2)	1
Tap water + 1% FA	0.0340(2)	5.0(2)	1.9
40% CuCl ₂	0.0032(2)	0.8(2)	19.6
40% CuCl ₂ + 1% FA	0.0024(2)	0.6(2)	26.1

3. Results and discussion

3.1. Flame extinguishment efficiency by aerosols of the CuCl₂ aqueous solutions

The graphic presentation of the fire extinguishing efficiency determination results using the CuCl₂-containing AFEA in an enclosed space is displayed on Fig. 3. As we can see on the plot, 3.5 cm³ of the sprayed 40% CuCl₂ aqueous solution is quite enough to extinguish the seat of fire of B₂ class (monoethanolamine). That is, fire-extinguishing ability of this solution is 11.3 times higher than fire-extinguishing ability of tap water. The same is observed when extinguishment results of flame for polar hydrocarbons (monoethanolamine) are compared with those for non-polar hydrocarbons (hexane). Here, the ability of the 40% CuCl₂ aqueous solution to inhibit monoethanolamine flame is 1.64 times higher than in the case of *n*-hexane flame.

In turn, the curves on Fig. 3 show clearly that the fire extinguishing efficiency of the AFEA depends directly on the amount of dissolved CuCl₂. At that, on the plot (Fig. 3) we have an almost smooth curve that can be precisely described by a square formula:

$$\frac{1}{V_{AFEA}} = a\omega + b\omega^2, \tag{2}$$

where V_{AFEA} is a volume of the AFEA expended on the flame extinguishment, ω is the mass fraction of CuCl₂ in aqueous solution, and a or b are the constants of equation.

It may readily be seen that if the concentration of CuCl₂ in the AFEA aerosol increases, then a time needed the flame suppression decreases, the amount of the expended aqueous solution of the AFEA reduces too. All these concern the extinguishment both *n*-hexane flame and monoethanolamine flame.

Attention is drawn to the fact that the AFEA containing a little amount of FA extinguishes the flame better than the same AFEA, but without FA. Fire extinguishing test results using the AFEA in an open space have showed that 40% aqueous CuCl₂ containing 1% FA suppresses flame 26.1 times more efficient than tap water and 1.3 times more efficient than 40% aqueous CuCl₂ solution without FA. Incidentally, the FA addition also increases the fire extinguishing ability

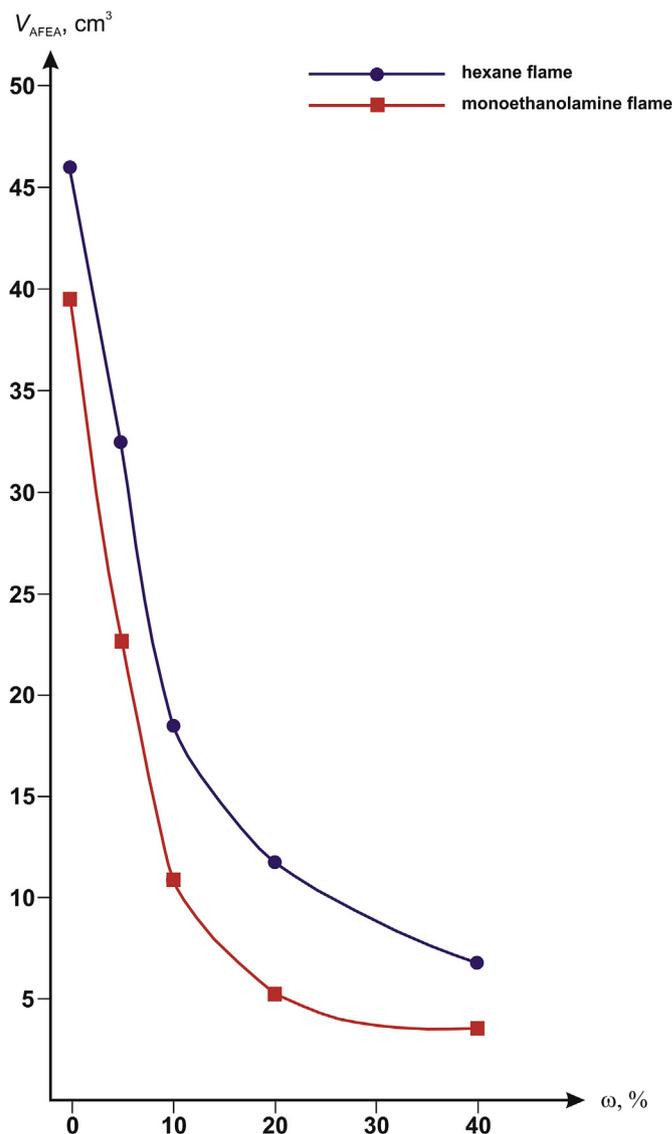


Fig. 3. The volume of the AFEA expended on the flame extinguishment versus the CuCl₂ concentration in aqueous solution.

of tap water (see Table 3). This can be explained by an increase of the Q_{AFEA} values, for after a surfactant addition the fluidity of the solution increases (see Table 1). Thus, it has been experimentally ascertained that a time needed to suppress the seat of fire of B₁ class in an open

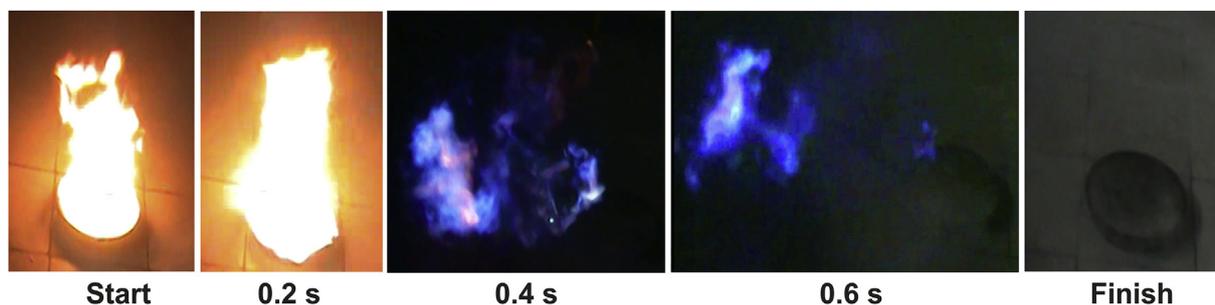


Fig. 4. The freeze frames of a video demonstrating the process of the extinguishment of the seat of fire of B₁ class in an open space by using the sprayed solution of the AFEA (40% CuCl₂ + 1% FA) (the step between the frames is 0.2 s).

space using the fire-extinguishing aqueous solution (40% CuCl₂ + 1% FA) was 0.6 s. For comparison, the duration of extinguishment the same flame by tap water was 9 s, and $\Delta\tau_{\text{extinguish}}$ for the 40% aqueous solution of CuCl₂ without FA was 0.8 s.

Stepwise visualization of the flame suppression process by the sprayed AFEA (40% CuCl₂ + 1% FA) is depicted on Fig. 4. In this photo, one can see clearly that in 0.2 s after the injection of the AFEA aerosol, the flame intensively blazes up. Apparently, at this stage of the inhibition reaction we deal with the interaction of gaseous molecules of copper(II) chloride with chemical radicals of flame, which is accompanied by the release of heat energy. In 0.4 s after start, the flame acquires a turquoise color that is attributed to the emission spectrum of Cu atoms, and in 0.6 s after start, the turquoise flame decays rapidly and then it disappears.

3.2. Hydrocarbon flame inhibition mechanism by the sprayed CuCl₂ aqueous solutions

The results obtained (see the previous section) contain valuable information that allows us to better understand the hydrocarbon flame suppression mechanism. It should be emphasized that when extinguishing a hydrocarbon fire with an aqueous solution of CuCl₂, the chemical effect of the additive dominates over cooling effect (or dilution effect) of solvent. Let's consider it in more detail. It is well known that copper(II) chloride evaporates easily at elevated temperatures, giving rise a thick brown smoke. At that, the gaseous copper(II) chloride is able to interact with different chemical radicals of the flame [28], forming complex adducts. Apparently such a behavior of the CuCl₂ aqueous solution in the flame determines the flame inhibition outcome. However, before proceeding to consider this mechanism, let us recall the flame structure and which chemical particles are in the flame.

A hydrocarbon flame is known to consist of three zones, which differ in temperature and the chemical nature of radicals [29]. In the first zone of the flame called the dark zone, there is an initial destruction of the combustible material. The temperature of the flame in this zone is the lowest, and the nature of the formed chemical radicals ($\cdot\text{C}_2$, $\cdot\text{CN}$, $\cdot\text{CO}$, $\cdot\text{CH}$, $\cdot\text{NH}$, $\cdot\text{H}$, etc.) is reductive. On the contrary, in the second zone of the flame, called the oxidation zone, the chemical radicals of the reductive nature are oxidized, forming CO₂ and H₂O, mainly due to the diffusion of oxygen from the atmosphere directly to the flame. That is why the temperature in this zone is the highest, and the nature of the chemical radicals ($\cdot\text{O}$, $\cdot\text{OH}$, NO \cdot , HCO \cdot , etc.) is oxidative. Finally, in the third zone, called the luminous zone, the heat and the combustion products leave out the flame by predominantly convective flows. The temperature of the flame in this zone is slightly lower than in the oxidation zone. At high temperature, chemical radicals and molecules radiate electromagnetic waves, coloring the flame [30]. The lengths of electromagnetic waves that radiate the corresponding chemical particles of the hydrocarbon flame are shown in Table 4.

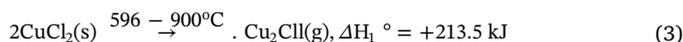
The 306.4 nm spectral band is generated by $\cdot\text{OH}$ particles

Table 4

Radiation spectra for some chemical particles of the hydrocarbon flame.

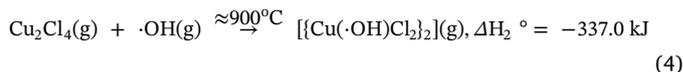
Species	λ , nm	Species	λ , nm
$\cdot\text{OH}$	306.4	HCO \cdot	250.0–400.0
$\cdot\text{NH}$	334.6	$\cdot\text{CH}$	430.0–438.0
$\cdot\text{CN}$	349.5–353.4; 387.0	$\cdot\text{C}_2$	467.0–472.0; 513.0–517.0; 559.0–564.0
$\cdot\text{H}$	396.3; 410.1; 434.0; 487.1; 656.3	H ₂ O*	591.0; 616.0–625.0
$\cdot\text{Cu}$	324.7; 453.1		

responsible to branch the chain reaction w flame (see Table 4). Once the CuCl₂ aqueous solution is sprayed above fire, complex physical-chemical processes which eventually interrupt chain reactions are immediately begun in the flame. Sequence of transformations of the CuCl₂-containing AFEA in the fire is shown in Fig. 5. At the first stage of the transformation (Fig. 5, stage 1), the spraying of liquid aerosol (CuCl₂ aqueous solution) over the flame causes an instantaneous water evaporation, absorbing a large amount of heat (43.94 kJ·mol⁻¹); at that a solid aerosol of CuCl₂ (thick brown smoke) is generated (Fig. 5, stage 2). These solid particles of copper(II) chloride in the oxidation zone of flame rapidly evaporate (Fig. 5, stage 3), absorb heat (213.5 kJ·mol⁻¹) and convert to Cu₂Cl₄ gaseous molecules:

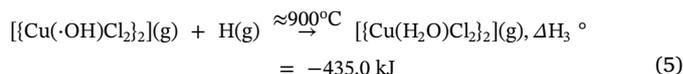


Unique spectroscopic studies were carried out in Ref. [31]. The authors of this article studied the stereo-chemistry of these Cu₂Cl₄ gaseous particles that have the form of flat molecules shown in the Scheme 1.

It can be expected that the appearance of the Cu₂Cl₄ discrete molecules in the flame will predetermine the final inhibition result. This assumption is based on an exceptional ability of the Cu₂Cl₄ plane fragment to bond with the HO \cdot chemical radicals in the flame. As a result of it, the radical-molecular adduct of $[\{\text{Cu}(\cdot\text{OH})\text{Cl}_2\}_2]$ is formed. All this is accompanied by the release of heat energy in the amount of 337 kJ per mole of the Cu(II)→($\cdot\text{OH}$) bonds formed:



Final deactivation of the chemical radicals happens owing to binding of the protons ($\cdot\text{H}$) with the $\cdot\text{OH}$ particles coordinated to Cu(II) centers. This generates the formation of the molecular aqua-complex of $[\{\text{Cu}(\text{H}_2\text{O})\text{Cl}_2\}_2]$ and the release of heat (435 kJ):



The stereo-chemical aspect of the Cu₂Cl₄ molecules interaction with the $\cdot\text{OH}$ and $\cdot\text{H}$ chemical radicals in the flame is shown in Fig. 6. It should be noted that the maximum possible number of coordination points for the Cu₂Cl₄ molecule is 4, i.e. 1 mol of Cu₂Cl₄ units can

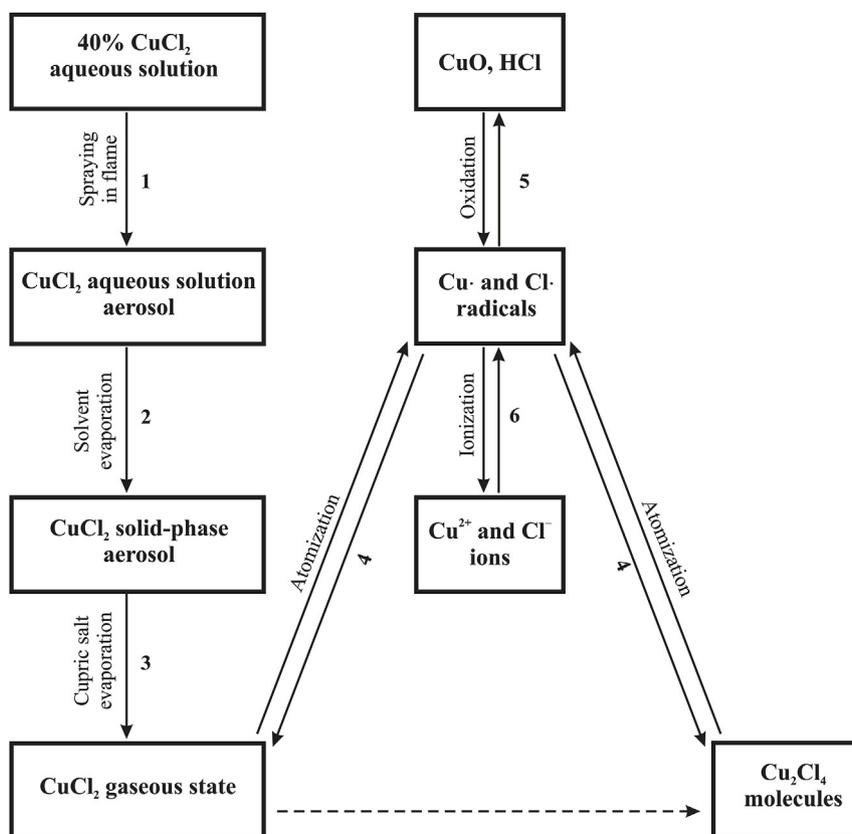
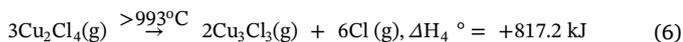


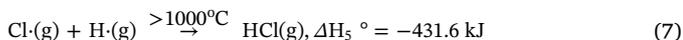
Fig. 5. The physical-chemical transformations of the aqueous solution of CuCl₂ in flame.

deactivate 4 mol of ·OH particles.

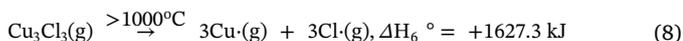
Next, the Cu₂Cl₄ molecules undergo the disproportionation under the influence of high temperatures (≈ 1000 °C) giving Cu₃Cl₃ and ·Cl [32]:



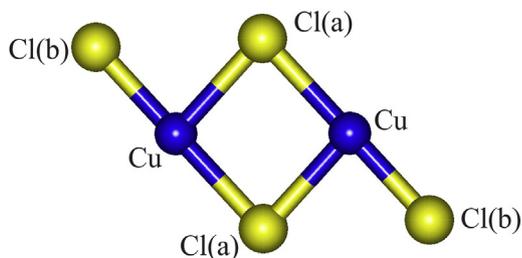
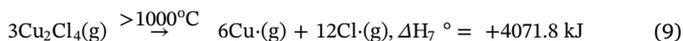
This oxidation-reduction process (see reaction 6) is endothermic and the atomic chlorine interacts instantly with atomic hydrogen, generating the HCl molecules with considerable heat release:



Next the Cu₃Cl₃ gaseous molecules break down above 1000 °C, giving the Cu· and Cl·:

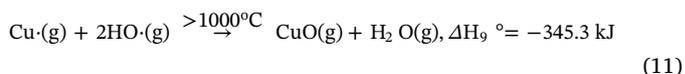
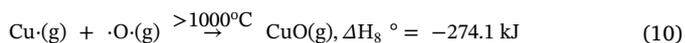


The total energy balance of reactions 6 and 8 gives an enormous amount of absorbed heat energy that takes place at the thermal decay of the Cu₂Cl₄ molecules (Fig. 5, stage 4):



Scheme 1. The Cu₂Cl₄ gaseous particle structure.

When the temperature of the flame reaches a mark of 2000 °C, the ionization processes for Cu· and Cl· atoms can be predominated (Fig. 5, stage 6). Yet, the probability of the exothermic process of Cu· atoms oxidation by chemical radicals of ·O· and HO·, and the formation of CuO product (Fig. 5, stage 5) is significantly higher:



4. Conclusions

Thus, the elaborated aqueous fire-extinguishing agent (AFEA), the 40% aqueous solution of copper(II) chloride, is the pretty efficient fire-extinguishment agent to inhibit the hydrocarbon flame. Under conditions of the experiment, the extinguishment duration of the seat of fire of B₁ class by the AFEA aerosol (40% CuCl₂ + 1% FA) is 0.6 s that is 26 times more efficient than the analogous extinguishment by the water aerosol. The least of the AFEA expense needed to total suppress the hydrocarbon flame was 0.034 L·m⁻² (the minimum water expense is

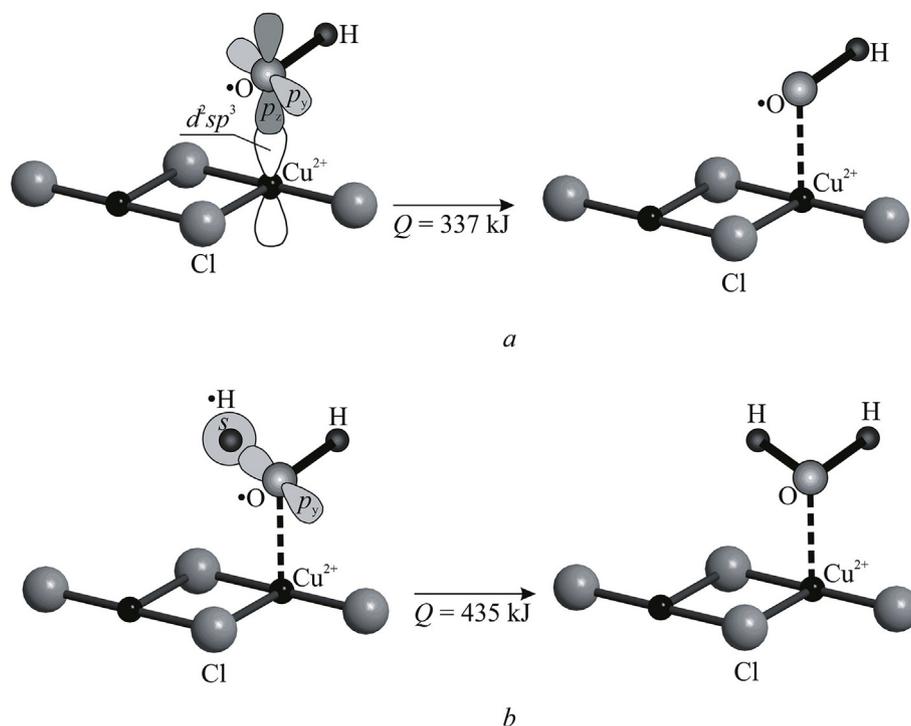


Fig. 6. The stereo-chemistry of the reaction 4 (a) and the reaction 5 (b).

$0.883 \text{ L}\cdot\text{m}^{-2}$; $I_{\text{AFEA}} = 0.057 \text{ L}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ ($I_{\text{water}} = 0.100 \text{ L}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$).

The analysis of information obtained when studying the fire-extinguishing properties of CuCl_2 -containing AFEAs enabled to uncover specific behavior features of copper(II) chloride aqueous solutions in the hydrocarbon flame. It made it possible to adequately interpret the suppression mechanism of hydrocarbon flame by aqueous solutions of copper(II) salts. This process is described by the associative mechanism: initially, an elementary act of interaction of the active radicals of the flame ($\cdot\text{OH}$ particles) and the Cu_2Cl_4 gaseous molecules with the formation of the radical-molecular complex takes place. Next the coordinated $\cdot\text{OH}$ groups are attacked by $\text{H}\cdot$ particles and, thus, deactivated. The described process is stereo-specific. In this process, coordinated O atoms of $\cdot\text{OH}$ particles are exactly that place where the stereospecific recombination of $\cdot\text{H}$ radicals occurs. As a result, the sequence of chain reactions in the flame is interrupted, and the combustion is ceases.

Studies directed towards the complementary experimental data obtaining to enable to unambiguously interpret the mechanism of the combustion inhibition of hydrocarbons by copper(II) salts aqueous solutions will be suggested in future. The results of these investigations will become the basis of future publications.

Conflict of interest

There is no conflict of interest.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.firesaf.2019.03.005>.

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