Practice of Use of Aerosol Extinguishing Agents Obtained by Combustion of Propellants

A N BARATOV
Moscow State Building University
Yaroslavskoye Shosse, 26, Moscow, Russia

N A BARATOVA
Gabar Enterprise
Krasny Kazanets str., 17-49, Moscow, Russia

Y A MYSHAK and **D Y MYSHAK**
Institute of Fire Safety
Ministry of the Interior of Russia
B. Galushkina, str., 4, Moscow, Russia

ABSTRACT

The research results of new agent for volumetric extinction are stated. The new agent is alternative to Halons and is obtained by combustion of propellant that consists of oxidant-reducer mixture. Inorganic oxygen-containing potassium salts are used as an oxidant and organic resins are used as a reducer. The gaseous atmosphere of aerosol that is obtained after combustion of propellant mainly consists of carbon dioxide and condensed phase mainly contains potassium carbonate. Aerosol possesses the highest fire control capability that is about one order more than Halon 1301 has and is low-toxic and ecologically harmless.

The disadvantages of the aerosol are its high extent of heating and the presence of open flame force. Experimental and theoretical results are stated to illustrate the decline of extinguishing properties of hot aerosol. To remove these disadvantages the special generators have been developed. The experimental results showed their high efficiency, reliability and safety in use for extinction of fires of different classes.

Aerosol Fire Extinguishing Agent (AFEA) is a new agent that is obtained by combustion of solid propellant composition (SPC) consisted of oxidant and reducer. Inorganic potassium salts are used as an oxidant and organic resins are used as a reducer. Aerosol that forms as a result of combustion of SPC contains mainly carbon dioxide in gaseous phase and mainly potassium carbonate and a small quantity of potassium oxides in condensed phase.

The idea of creation of aerosol fire extinguishing agent emerged from the experience of work in the field of dry-powdered chemicals. It is known that the more finely divided is the powder (i.e. the more is its dispersity), the more is their ability to fire extinction. However significant increase of powder dispersity is limited due to sharply increasing propensity to caking and lumping and due to significant increase of technical and technological difficulties and cost of production of finely divided powders. Desire to have the most finely divided dry-powdered chemical in the moment of fire origin brought to the idea of "smoke pot" that is receiving of powder in form of aerosol obtained by combustion of solid propellant composition (SPC).

In accordance with [1] the most effective are dry-powdered chemicals based on inorganic potassium salts. Therefore potassium nitrate (KNO_3) was chosen as an oxidant. Different organic low-volatile substances may be used as reducers. We chose epoxy resin ED-20. Correlation of SPC components in the composition of TTK-4 was determined from stoichiometric equation that corresponds to interaction between resin and potassium nitrate. Correlation between components in the TTK-6 composition was determined with regard to some fuel excess. This is aimed to obtain AFEA with increased ability to extinguish Class A fires (smoldering materials: wood, paper, textile and the like). More detailed these problems are considered below.

Composition of aerosols that were obtained as the products of combustion of these solid propellant compositions contains:

- in gaseous phase: carbon dioxide (CO_2), water steam (H_2O), nitrogen, negligible quantity of potassium hydroxide (KOH) and traces of carbon monoxide (CO) and nitrogen oxides (N_xO_y);
- in condensed phase: potassium carbonate (K_2CO_3), potassium bicarbonate ($KHCO_3$) and a small quantity of potassium oxide (K_2O).

Mass relation between gaseous and condensed phases is 1:1.

Characteristics of SPC are presented in Table 1.

TABLE 1. Characteristics of solid propellant compositions

Characteristic	TTK-4	TTK-6
Density, kg/m^3	1.7	1.65
Linear rate of combustion, mm/s	1.8	1.2
Barometric index of rate of combustion, ν	0.45	0.4
Combustion temperature, K	1550	1480
Ignition temperature, K	810	780

Barometric index ν does not exceed 0.5 in equation that determines dependence of rate of combustion on pressure $U=Ap^{\nu}$. This fact points out less probability that SPC combustion transforms into explosion at moderate pressure rise.

Explosion safety of SPC is confirmed by the special investigations performed in the Institute of Chemical Physics of Russian Academy of Sciences. Characteristics of aerosol compositions obtained by combustion of TTK-4 and TTK-6 and their comparisons with the other agents of volumetric extinction are presented in Table 2.

Analysis of Table 2 shows that AFEC has the highest fire control capability out of all extinguishing agents (fire-extinguishing concentration of AFEC is 5-8 times less than of Halon 1301), low toxicity, absence of ozone-depleting effect and is cost-effective. The lower cost of protection by means of AFEC is caused by the fact that use of AFEC in contrast to the other agents does not claim pressure vessels and pipeline systems.

TABLE 2. Characteristics of aerosol fire extinguishing agents (AFEA) in comparison with the other agents of volumetric extinction

Characteristics	AFEA		CF_3B_2	CO_2	Dry chemicals	C_4F_{10}*
	TTK-4	TTK-6				
Fire control capability, kg/m^3						
• Classes A2, B, C fires	0.05	0.05	0.3	0.7	0.25	0.5
• Class A1 fires	-**	0.8	-***	-***	-***	-***
Toxicity, mg/m^3	>10	>10	>10	>10	>10	>10
Ozone-depleting effect, relative units	0	0	10	0	0	0.1
Cost of 1 m^3 protection, USD	5	5	20	20	10	25

** Compounds with use of C4F10 are adopted by USA Standard 2001 as alternative to Halons*
*** Only localize*
**** Don't extinguish*

Analysis of Table 2 shows that AFEC has the highest fire control capability out of all extinguishing agents (fire-extinguishing concentration of AFEC is 5-8 times less than of Halon 1301), low toxicity, absence of ozone-depleting effect and is cost-effective. The lower cost of protection by means of AFEC is caused by the fact that use of AFEC in contrast to the other agents does not claim pressure vessels and pipeline systems.

Automatic start of the protection system with AFEA may be performed by means of existing automata's systems and in the absence of special devices or electricity it the may be performed directly from fire site (the system that has a such kind of start is offered to name "autonomous"). It should be noted that as it is shown below "Gabar" organization developed such composition and devices that as opposed to all other agents of volumetric extinction provide extinction of Class A1 fires. The fires of such class always present in the real fire scenario (building constructions and lining materials, paper, textile and the like). Thus AFEA is the best alternative to Halons that are harmful for ecology.

Volumetric fire extinction by means of aerosol is shown in the scheme in Fig.1.

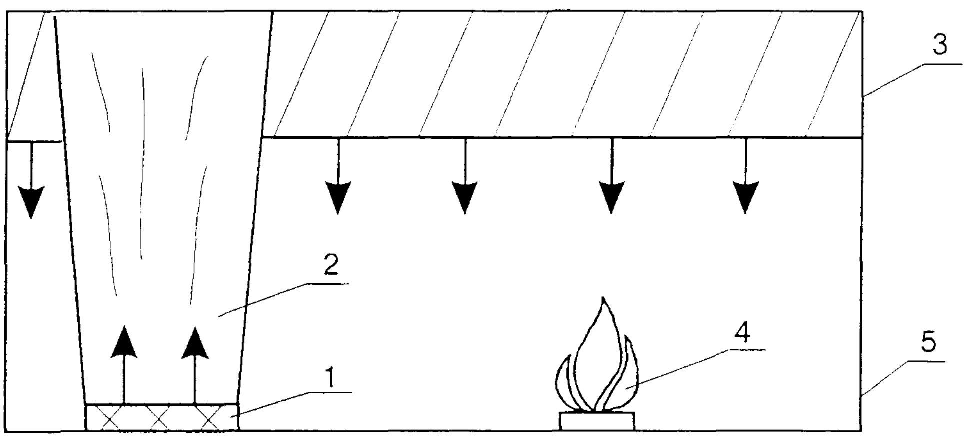

FIGURE 1. Scheme of aerosol fire extinction: 1 - charge of SPC; 2 - flow of AFEA in the period of its formation (combustion of SPC); 3 - heated layer of AFEA (arrows show how the cloud of AFEA descends in the process of cooling); 4 - fire origin; 5 - protecting premises

Convective ascent of AFEA in the period of its formation is caused by the high degree of its heating up.

As for extinction mechanism of AFEA it should be noted that the main contribution to fire extinction effect is performed by condensed phase. Gaseous phase has only diluent action. When flame is exposed to AFEA, inhibitions of combustion play the dominant role in this mechanism, as flame quenching by a such small quantity of aerosol can't be explained by heat elimination from the flame. It is known that to stop combustion about 40% of energy must be taken of the flame. Elementary calculation shows that when concentration of AFEA corresponds to extinguishing concentration, heat losses (heating up, evaporation and decomposition of aerosol) take negligible part of the losses that are required for extinction of flame.

Inhibition of flame is performed by means of combined heterogeneous - homogeneous mechanism. Heterogeneous inhibition is connected with recombination of active centers (radicals and atomic particles), that are responsible for origination and development of combustion process, on the surfaces of aerosol solid particles. The mechanism of recombination may be schematically described as follows:

$A + S \rightarrow AS$

$AS + A \rightarrow A_2 + S$ and so on,

where A - active center; S - solid surface.

Fig. 2 shows the dependence of fire control capability for different salts on the values of heterogeneous recombination coefficient for oxygen atoms on the surface of these salts. Oxygen atoms are one of the most active centers in the flame.

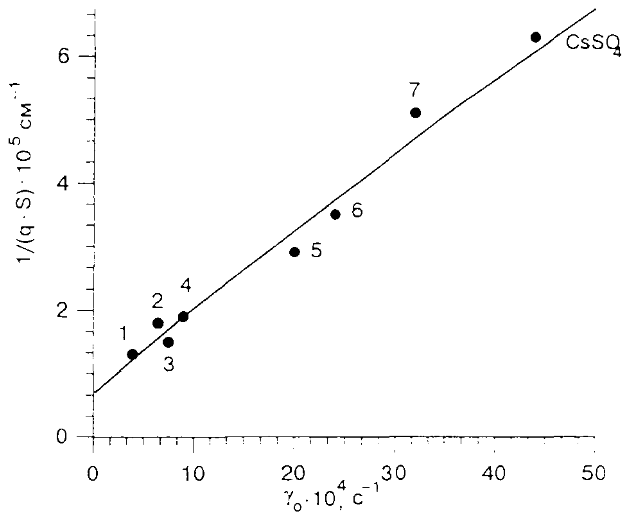

FIGURE 2. Dependence of fire control capability for salts on the values of heterogeneous recombination coefficient for oxygen atoms on the surface of salts: 1 - Na_2O_3; 2 - $(NH_4)_2C_2O_4$; 3 - Na_2SO_4; 4 - $NaHCO_3$; 5 - KCl; 6 - $KHCO_3$; 7 - $K_2C_2O_4$

Since destruction of active centers on the surface of solid particles is proportional to the surface of particles the fire control capability was characterized by inverse product of extinguishing concentration (g, kg/m^3) and specific surface area of salt (S, m^2/kg).

As it may be observed from Fig.2 the dependence between ($1/(q \cdot S)$) and ($\gamma_{O,H}$) is cymbate and shows that when coefficient of heterogeneous recombination of active centers increases fire control capability of salts also increases. In this case salts that had potassium as a cation were found to be more effective than sodium salts. It is interesting that cesium and rubidium salts were found to be much more effective However their application is problematic due to their high price and some other peculiarities. Based on these data such formula for SPC has been chosen that its combustion results to formation of potassium compounds.

As it may be observed from Table 2 fire control capability of AFEA is approximately one order more than of dry chemicals that have the same composition as condensed phase of AFEA. As it was noted above this phenomenon is caused by the fact that solid particles of AFEA have the higher dispersity. In accordance with [1] the following interrelation exists between extinguishing concentration of solid particles of salts and the velocity of hydrocarbon flame propagation (U_f):

$$g \sim rU_f^2,$$

where r - radius of solid particles.

Since extinction of flame is characterized by decrease of flame velocity it may be seen that flame control capability of solid particles is inversely proportional to square root of particles size. Commonly used dry chemicals have particles with the size of 40-80 μm. For aerosol the size of solid particles is about 1 μm. Thus fire control capability of AFEA is one order higher than of dry chemicals. This analysis that is based on heterogeneous mechanism satisfactory agrees with the presented above properties of AFEA and therefore confirms the applicability of this mechanism to fire extinction by means of AFEA.

However as it is shown in [1] when the size of the powders is less than 10 μm they managed largely to evaporate in flame. In this case the contribution that gives the homogeneous inhibition mechanism of aerosol combustion should be taken into account. In accordance with [2] homogeneous inhibition mechanism is performed as follows:

$KOH + H = H_2O + K;$

$KOH + OH + H_2O + KO;$

$K + OH + P = KOH + P.$

In this process P takes part as the third particle in reactions of chain stopping. Validity of this mechanism is confirmed by study [3] where antagonism effect in the process of simultaneous action on the flame of potassium chloride and diammonium phosphate is revealed. This effect is expressed by the fact that consumption of salts is more at joint use of KCl and $(NH_4)_2HPO_4$ than in the case when they are used separately. The antagonism was found out is caused by removal of KOH from the inhibition process due to reaction $KOH + HPO_3 \rightarrow KPO_3 + H_2O$. Thus combined inhibition of the aerosol combustion is confirmed. However, we consider that the heterogeneous mechanism plays predominant role.

Together with a row of advantages AFEA has tow significant disadvantages:

- high extent of aerosol heating up;
- presence of strong force of open flame at combustion of SPC.

The first disadvantage causes delay in time for fire extinction and increases losses of AFEA through non-compactness. Science as it may be seen from Fig. 1 hot aerosol rises to the ceiling of protected compartment due to convection and only after cooling reaches fire origin. The second disadvantage does not permit to use AFEA for protection of explosion dangerous premises where dangerous explosion mediums may be formed due to that or another reason. Besides flame force may cause fire in the case of accidental ignition of SPC.

To overcome these disadvantages the "Gabar" organization developed special devices that provide cooling of aerosol and removal of the open flame force. Currently the generators of "Gabar-P" type are in wide use. They are thin-walled metal vessels that are put in each other and that perform the principle of hydraulic seal.

Side walls of the vessel 1 are equipped by shirts 3 that provide the creation of insulated cavities. The ablation powder that provides effective cooling of aerosol flow is poured into these cavities. The additional cooling is reached by means of creation of hydraulic seal that is of cooling powder 5 on the way of aerosol movement 7.

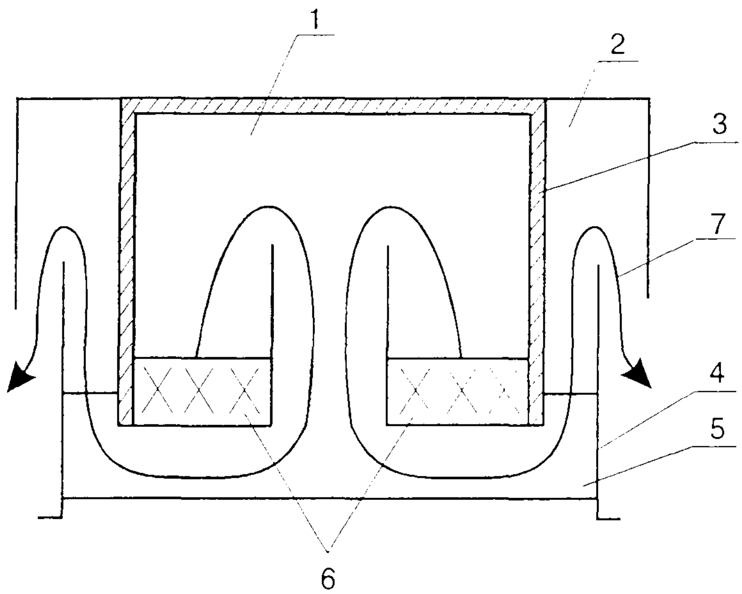

FIGURE 3. Scheme of generator "Gabar-P": 1- inner vessel; 2- cover; 3- cavities that are filled by cooling powder; 4 - outer vessel; 5 - layer of cooling powder; 6 - charge of SPC; 7 - way of AFEA flow movement

When cooler is chosen the following demands are claimed:

- low temperature of decomposition;
- comparatively high exothermics of decomposition;
- absence of toxic and corrosive decomposition products;
- low cost and accessibility.

As a result of special investigation the powder on the base of one of carbonic acid salts was chosen as the such cooler.

Characteristics of generator "Gabar-P" that working principle has been patented [4] are presented in Table 3.

TABLE 3. Characteristics of generator "Gabar-P"

Characteristic	Gabar-P2	Gabar-P6	Gabar-P1
Diameter/height, mm	300/365	590/535	590/535
Mass of charged generator, kg	15.5	51.5	61.5
Temperature of AFEA at the outlet, °C	200	140	160
Temperature of shell, °C	140	90	150
Operation time, s	30±10	35±10	40±10
Protecting volume, m^3	20 (40)	65 (130)	105 (21

These generators were repeatedly successfully tested. The results of comparative tests of generator AFEA that are manufactured in Russia by different firms [5] are presented in Table 4 and Fig. 4 and 5. These tests were executed in the room with the volume of 64 m^3 and the height of about 3 m that failure of sealing was characterized by the net surface of openings to the room volume and was 0.025 m^{-1}. Two fire sites were extinguished simultaneously: 13V and 5A. The time of free combustion was 60 s for fire 13V and 180 s for fire 5A. The temperatures in the region of fire sites were measured with the help of thermocouples.

TABLE 4. Comparative tests of AFEA generators

Designation of generator	Manufacture	Total mass of charge	Number of generators	Test results
Gabar-P6	"Gabar" organization	5.5	1	Both fires are suppressed
SOT-5	Joint-Stock Company "Granit"	6.0	2	Fire 13V is suppressed, fire 5A is not suppressed
MAG-4	Scientific-Industrial Union "Soyuz"	5.8	6	– " –
Purga-M-1.2	Scientific-Industrial Union "Soyuz"	6.0	4	– " –
OR-273	Plant, Perm	5.4	3	– " –
GOA-3M	Joint-Stock Company "Tekhnolog"	5.8	4	– " –

These results show that when the discharge of SPC is approximately the same that is about 0.1 kg/m^3 the fire 13V was suppressed by all tested generators and only generator "Gabar-P6" suppressed fire 5A.

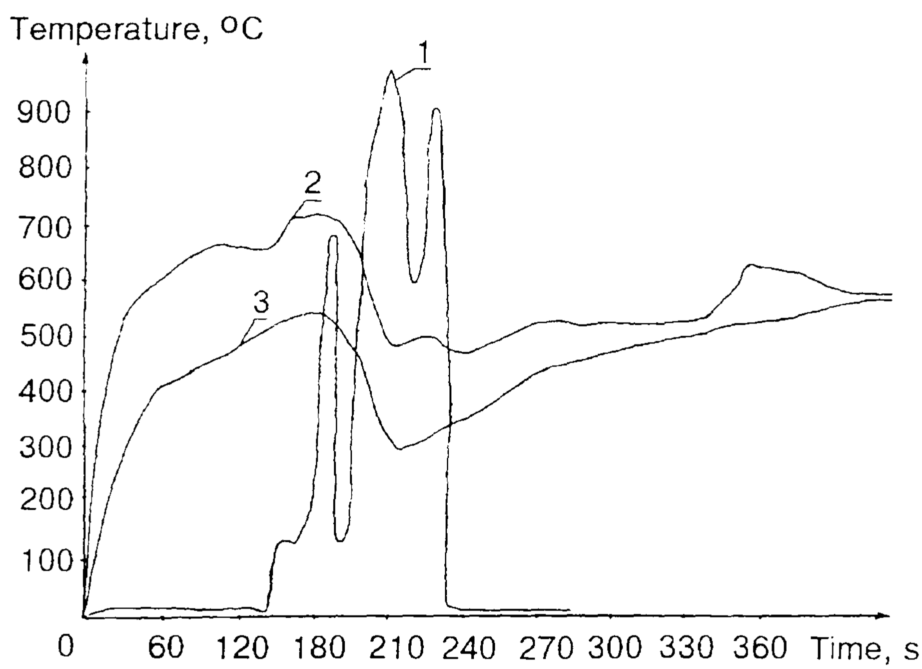

FIGURE 4. Thermogram obtained in test with generator "SOT": 1 - temperature above the fire 13V; 2 - temperature inside the fire 5A; 3 - temperature above the fire 5A

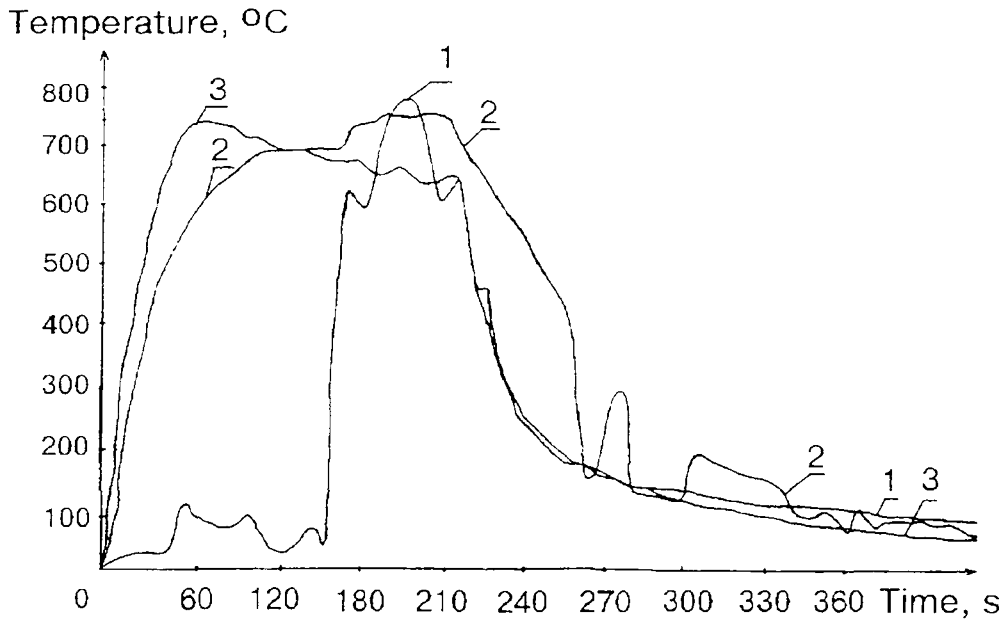

FIGURE 5. Thermogram obtained in test with generator "Gabar": 1 - temperature above fire 13V; 2 - temperature inside fire 5A; 3 - temperature above fire 5A

Thermograms in Fig. 4 and 5 show that during suppression of fire 5A some drop of temperature in the fire site took place after the generator "SOT-5" started to operate and then the fire flamed up again. When this fire site was suppressed by generator "Gabar-P6" the temperature in fire site consistently reduced till room temperature. Successful suppression of the fire 5A was caused by the use of cooled AFEA that was obtained after combustion of specially developed for suppression of smoldering materials TTK-6.

TABLE 5. Generalized test results

Date of test	Test conditions	Type of generator	Test results
29.09.93	Joint-Stock company "Elinar", Moscow Region, paint and varnish workshop, not fully sealed volume V=250 m^3, 3 fires with acetone at different levels	"Gabar-P10"; 3 generators; total mass of TTK-4 - 25 kg	Productive time of generator - 40 s. All fires were suppressed before the end of AFEA discharge. Temperature on generator's shell ≤ 110°C
22.11.93	Trade booth in Moscow, V=30 m^3, fires: gasoline at F=0.05 m^2; package, shavings with the mass of 10 kg at F=1.5 m^2; time of flaming up - 60 s, 3 tests	"Gabar-P1" (without cooler) with charge mass of 1 kg; 2 generators	Virtually instantaneous suppression of gasoline fire. Suppression time of fire A1 is about 30 s without repeated flaming up. Fire-extinguishing concentration is about 0.067 kg/m^3. The results of every of 3 tests are the same

Continuation Table 5

20.04.93	Institute of Chemical Physics of Russian Academy of Sciences. Explosion safety of compositions TTK-4 and TTK-6	Without generators	The dependence of rate of combustion (U) on pressure (P): $U=AP^{v}$, is obtained. Value of barometric index v < 0.5, that is transition of combustion to explosion is impossible when P less 0.1 MPa
08.08.94- -16.08.94	Acceptance tests of generator "Gabar-P6"; VNIIPO; V=65 m^3; failure of sealing - 0.01 m^{-1}; fires: 13V, 5A and A2 (rubber, cable)	"Gabar-P6" with TTK-4 and TTK-6	Reliable suppression: of fires 13V and A2 with fire-extinguishing concentration 0.046 kg/m^3; of fire A1 with fire-extinguishing concentration 0.1 kg/m^3; temperature of AFEA < 200°C; pressure in room ≤ 1
	Explosion safety of stoichiometric propane/air mixture	"Gabar-P6"	The ignition of mixture at switching of the generator did not occure in 3 tests after holding of in propane/air mixture during 24 hours
	Certification tests of VNIIPO, V=120 m^3; failure of sealing - 0.025 m^{-1}; fires 13V	"Gabar-P6"; 2 generators	Successful fire suppression in all tests. Temperature of AFEA at the distance of 0,05 m from the outlet of generator ≤ 80°C
20.05.95- -22.05.95	V=50 m^3; fire origin: oil for transformers and 5A	"Gabar-P6"; 1 generator	Reliable suppression in 3 tests

Besides tests on inhibition of explosion dangerous gas- and powder mixtures with the help of AFEA were performed.

Comparison between these test results and traditional agents is presented in Table 6.

TABLE 6. Comparison between test results and traditional agents

№	Test conditions	Fire-extinguishing concentration, kg/m^3			Notes
		AFEA	Halon 1301	Dry chemical	
1	Hydrogen/air mixture percentage (% by vol.): • H_2 - 10, air - 90; • H_2 - 20, air - 80	 0.07 0.23	 0.87 1.38	 0.38 0.77	Russian Standard GOST 12.1.044-89 ("peak" concentrations)
2	Stoichiometric propane/air mixture	0.04	0.3	0.25	
3	Dust/air mixture solidified by epoxy resin	0.088	-	-	Chamber, V=0.25 m^3

The successful suppression of Class A1 fires by means of generator 'Gabar-P" is confirmed also by certification tests that have been executed in Czechia in 1966 and is illustrated by the plot in Fig. 6. However, it should be kept in mind that suppression of Class A1 fires by means of generators "Gabar-P"-type is reached, when free burning time is less than 3 min. When fire 5A began to flame up during 5 min, the suppression did not been reached.

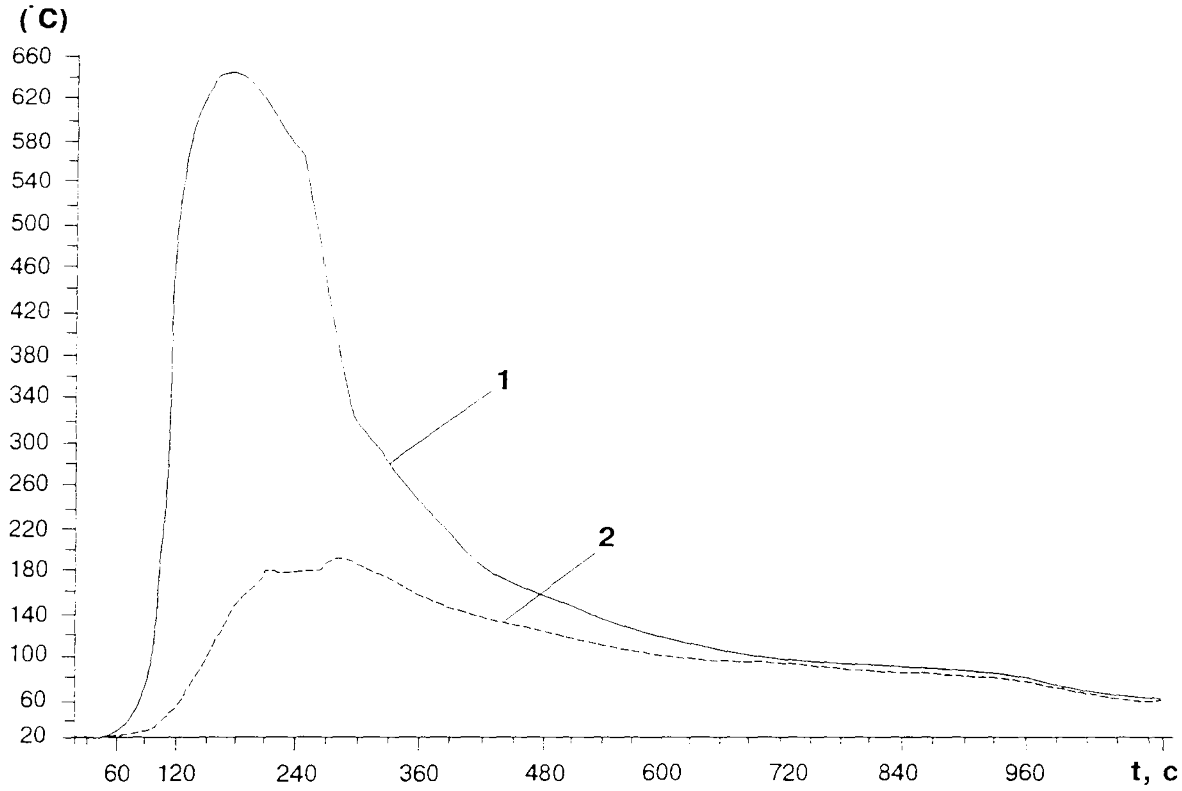

FIGURE 6. Thermogram obtained in test with generator "Gabar-P6" during suppression of fire 5A: 1 - temperature in fire site; 2 - temperature of AFEA on the outlet of generator

The generalized results of different tests of generators "Gabar-P"- type that confirmed high efficiency and reliability of these generators are presented in Table 5. Besides generators "Gabar-P", "Gabar" organization developed two more ways to obtain cooled AFEA and proper tools: ejection tool lie in the fact that incandescent aerosol flows combine with cooling liquid; and bubbling tool lie in bubbling of aerosol through the liquid layer. The more perspective both these tools are for protection of tanks with petroleum products. Schematically ejection tool is shown in Fig.7.

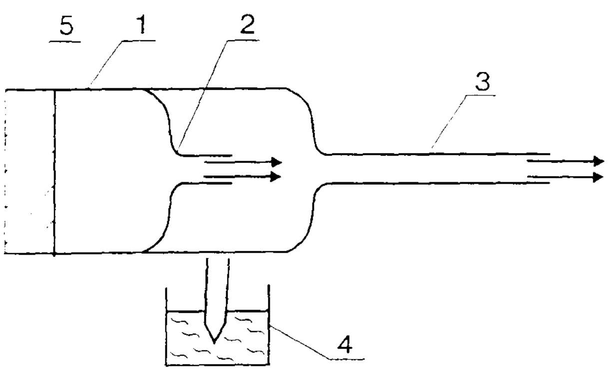

FIGURE 7. Scheme of ejection generator: 1 - combustion chamber; 2 - profiled nozzle; 3 - mixing chamber; 4 - vessel with cooler; 5 - TTK charge

Incandescent aerosol that outflows from the combustion chamber 1 create rarefaction in chamber 3 and draw in cooler from vessel 4. Mixture of aerosol and finely divided cooler outflows through the diffuser. Saturated water solution of inorganic salt is the more expedient for use as a cooler. For this case freezing temperature decreases and solubility of aerosol in cooler significantly reduces in comparison with water.

Generators "Gabar 7-0.5" that were developed in accordance with given principle have been tested using the mock-up of the tank with stationary roof with the volume 10 m^3. Gas condensate with flash point minus 42°C that was poured in the mock-up tank with the volume 3 m^3, was used as a fuel. On the side surface under tank roof two generators with the total charge 0.5 kg were assembled. Free burning time for condensate was 60 s. After generators were switched off by remote control, their operation continued for about 30 s. Stop of burning occurred in 20 s after generators were switched off, that is 10 s earlier than TTK charges in generators finished to burn. The result of repeated tests was the same.

In 1995 similar tests with the tank having the volume 1000 m^3 and the diameter about 11 m without roof have been conducted. Four generators "Gabar-E 20" where condensate was poured till the lower mark of the tank, were used in tests. Fire suppression was reached in 15 s after generators were switched off.

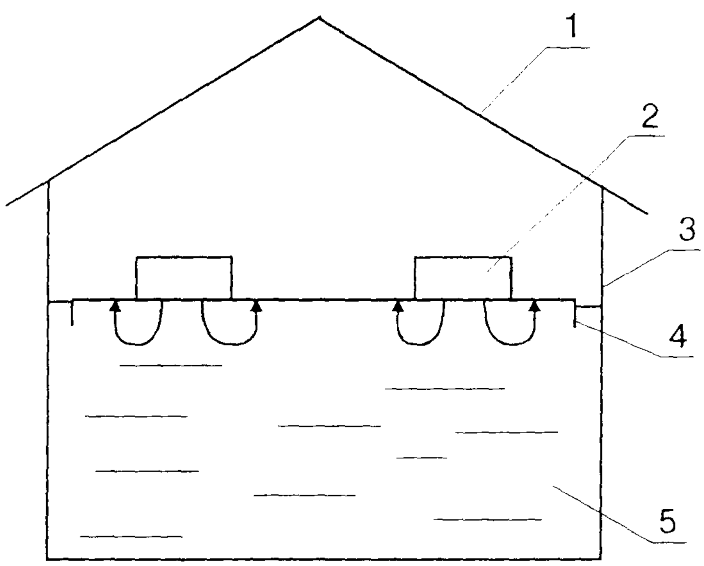

FIGURE 8. Scheme of protection by means of bubbling tool: 1 - stationary roof of tank; 2 - shell of tank; 3 - AFEA generators; 4 - pontoon or floating roof; 5 - petroleum product

Bubbling tool till was not tested. Ii is considered that to use generators "Gabar P" for this tool, that are arranged on pontoon (floating roof) is the more convenient way (Fig.8).

Current interest to the new methods of tank protection depends on the fact, that existing methods based on foam remain low-effective. In accordance with [8] for the 1978-1988 period 27 tank fires occurred in Tomsk region of Russia. All tanks were equipped by automatic foam extinguishing installations, but no one fire was suppressed. Estimated value of existing and suggesting ways of protection show, that expenses of aerosol protection of tank RVS-5000 do not exceed 70% of existing protection expenses.

The problems concerning validation of design recommendations for aerosol fire extinguishing systems and in particular determination of non-hermeticity of real compartments are among the sharpest scientific and technical problems of aerosol fire extinguishing. Analysis of norms passed in Russia [9, 10] show that after adoption of rational admissions the mass of using for fire suppression SPC twice exceeds fire-extinguishing concentration of AFEA pointed in Table 2. This norm is confirmed by numerous tests and therefore we included it in Table 3. The whole problem of non-hermeticity requires further study.

REFERENCES

1. Baratov, A.N., and Vogman, L.P. "Ognetushashchiye Poroshkovie Sostavy", M., Stroyizdat, 1984.
2. Baratov, A.N., and Ivanov, Ye.N. "Pozharotushenie v Khimicheskoi Promishlennosty", M. Izd. Khimia, 1979.
3. Tropinov, A.G., et al. "Vzaimodeistvie Smesei Diammoniifosfata i Khlorida Kaliya s Aktivnymi Radikalami Plameni Geptana. Kinetika i Kataliz", t.29, N 3, 1988, s. 425-527.
4. Patent RF, po zayavke N93043940, opublikovan v Byulletene Izobretenii N 26 za 1997 g.
5. Baratov, A.N., and Myshak, Yu.A., "Problemy Aerozolnogo Pozharotusheniya", Pozharovzryvobezopasnost, N 2, 1994, s.53-59.
6. Baratov, A., Myshak, Yu., and Damec, Y.: "Vyvojapouzifi haseni aerozoleni", Y. 150 Hori, N 6, 1994, p. 8-9, Chekhia.
7. Patent RF, po zayavke N93043940, opublikovan v Bulletene Izobretenii N 25za 1997 g.
8. Bezrodny, I.F., et al. "O Provedenii Sovmestnykh Issledovanii Sistem Protivopozharnoi Zashchity Rezervuarov i Rezervuarnykh Parkov", Otchet VNIIPO, 1988.
9. NPB 21-94 "Sistemy Aerozolnogo Tusheniya Pozharov. Vremennie Normy i Pravila Proektirovaniya i Ekspluatatsii", MVD RF.
10. "Avtomaticheskie Ustanovki Aerozolnogo Pozharotusheniya. Pravila Proektirovaniya i Ekspluatatsii", Proekt Norm NPB-1997, VNIIPO, 1997.