RESEARCH INTO EQUILIBRIUM AND NONEQUILIBRIUM PRESSURES IN THE FIRE EXTINGUISHERS CHARGED WITH GAS-LIQUID SOLUTIONS

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ABSTRACT

The efficiency of the fire extinguishing systems (FES) depends in great extent on the fire extinguishers (FE) charge norms tradeoff (charge density of the agent and gas-propellant pressure). Most of the aircraft and helicopter modules protected against fire are blown through with high flow rate air, so the FE pressure at maximum operating temperature shall approach the FE maximum operating pressure but not exceed it. It is known that a FE has a relief valve to prevent FE failure as a result of an uncontrollable rise of the FE pressure. The valve opening pressure is by 25-40% higher than the FE operating pressure. Review of both the Russian and American instructions, manuals and specifications has shown that the FE pressure–temperature relation (control of pressure points) is usually given for the equilibrium state of the saturated gas-Halon solutions. Nevertheless, in the course of operations, the cases of forming the nonequilibrium state (i.e., unsaturated solution, e.g., with a quick warming-up of the FE) are possible. If this is the case, the FE pressure can exceed the equilibrium pressure by 1.5 times. The paper presents the research into the dynamics of FE pressure development and the equilibrium state in relation to the FE state of fullness, agent properties, gas-propellant solubility factor and gas-liquid solution warming-up rate.

INTRODUCTION

All instructions and manuals, depending on the operating temperature, give pressures in fire extinguishers (FE) charged with gas-liquid solutions only for saturated solutions (e.g., [1-3]). Tables and diagrams of these documents specify the minimum pressure value in the bottles, i.e., saturated solution pressure, for each temperature. The only exception when unsaturated solutions are mentioned indirectly, is the description of the charge process. To attain the stable pressure when charging FEs, it is recommended to rock, shake, or turn over the fire extinguishers. Each operator knows that when pressurizing a FE charged with a fire suppression liquid, by a gas-propellant (nitrogen or air), the pressure rises beyond the nominal pressure but when shaking the FE, the pressure falls and reaches the equilibrium state. Then in the course of FE operation, in particular onboard the aircraft, in rather a wide temperature range, it is apparently implied that the pressure corresponds to the saturated solution. But this, in a great extent, does not correspond to the real situation. The solution in the FE can reach various states of unsaturation when temperatures vary, and this is the cause of pressure rise by 1.5 times and higher in comparison with the reference value. But is it a cause for worry since this event has temporary character? Is the pressure rise associated with any danger or can it be neglected?

In spite of all differences between the US and Russian FE parameters, a comparative analysis of specifications shows a lot in common. For example, the FE bottles charged with the primary fire extinguishing agent (Halon 1301 in the US aviation systems) shall meet the following requirements of active MIL--- : "....container should have a proof pressure of 9.62 MPa, a burst pressure of 12.37 MPa, and a frangible disc that will rupture at a pressure between 8.59 MPa and 9.62 MPa"[4]. As per requirements of NFPA-12A [13, the FE charge pressure at room temperature of 21 °C is 4.24 MPa, and for the recommended Halon 1301 charge density (1.121 kg/l or smaller, i.e., with a coefficient of volumetric filling **KV** = 0.71 or smaller) "as permitted in this standard, a pressure 7.27 MPa would be developed."

Now let **us** review similar parameters of the Russian FEs. According to a definition given in [5], "maximum internal pressure, which is developed by the normal run of the operation process, is called the operating pressure." For the Russian aircraft and helicopter fire extinguishing systems, "RD&PE Zvezda" JSC has developed Type 1 fire extinguishers with spherical bottles of 2-, 3-, 4-, 6- and 8-liter capacity, and Type 2 fire extinguishers with cylindrical bottles of 5, 8, 10, 16 and 20-liter capacity. According to the Operator's Manual [3], "the operating pressure in these FEs is 14.7 MPa and it is the design pressure at the maximum temperature." To charge the FEs, the charge nut was used including the frangible disc, which will rupture when the FE pressure rises to 19.6 ± 2.0 MPa, i.e., at a pressure between 17.6 and 21.6 MPa. These FEs are charged with Halon 2402, the main agent used in the Russian aircraft and helicopters since the 1960s [6], as well as Halons 1301 and 1211. The charge density of Halon 2402 is 2.415 kg/l, i.e., kV=0.65. The charge pressure for nitrogen and air is 8.8 MPa at the room temperature. Such charging has made use of the bottle strength capabilities since at the maximum operation temperature of 80 "C for Type 1 and 2 fire extinguishers, the maximum pressure of saturated solution 14.0 MPa was approaching the operating pressure 14.7 MPa, and at the minimum operation pressure of -60 °C, the FE pressure of 6.7 MPa provided for sufficiently high pressure of the agent in the ring manifolds to effectively suppress fire in the protected modules.

It is convenient to use relative units for comparison of typical FE pressures if we take the operating pressure equal to 1 as the reference (Table 1).

Table 1.

Pressure	MPa		Relative	
	USA	RUSSIA	USA	RUSSIA
1	2	3	4	5
Operation	7.27	14.74	1.0	1.0
Charge	4.23	9.83	0.58	0.66
Frangible disc rupture	8.59-9.62	17.7-21.6	1.18-1.32	1.20-1.46
Burst	12.37	38.3	1.7	2.6

Relative values of pressures given in columns 4 and 5 (Table 1), show a close level of pressures, first of all (that is important in this paper), for high pressure safety devices such as frangible discs, spring valves, etc. As follows from the table, the pressure rise above the operating pressure even by 1.2 times, and especially by 1.4-1.5 times, results in FE unsanctioned operation with the loss of fire extinguishing agent and environmental pollution.

This paper presents the test results showing the temporary rise level of the pressure above the operating pressure by unsaturation (disturbance of equilibrium) of gas-liquid solution.

METHODS

The research has been done using the flight aircraft FEs of Type 1 (2 and 3 liter) and Type 2 (8 liter). The FEs have been charged primarily with Halon 1211 produced by the Russian

Scientific Center "Applied Chemistry" according to TY 6-02-1103-82, grade 1, and also with Halons 2402 and 1301, and have been pressurized with air and nitrogen dried to the dew point of -40 °C. In accordance with the Technical Specifications, Halon 1211 contained 99.96% by volume of the main product, 0.01% by volume of air and 0.001% by mass of water.

The bottle capacity has been defined taking into account the difference in mass between an evacuated bottle and a distilled water filled bottle at the known temperature using a SARTORIUS balance with a 16 kg scale and 0.1 g scale division. The charged FEs have been put in an **ILKA** thermal chamber of 1-m^3 capacity where the temperature was set in the range from -70 to 100 "C. Using an adapter, valve, and connecting copper tubes of 1 mm in inner diameter and up to 3 m in length, the FEs were connected to the 250-kgf/cm^2 (245-MPa) scale pressure gauges installed outside the thermal chamber. The FEs capacity was registered taking into account design capacities of the adapters, valves, pressure gauges, and connecting tubes. The thermocouples made of chromium-nickel alloy and alumel were attached to the FE body with a fiberglass tape. The leads were brought out to a potentiometer located outside the thermal chamber. The mass of halon and gas-propellants (air or nitrogen) were defined by subsequent weighing on the SARTORIUS balance.

For forced mixing of the FE solution, the thermal chamber was provided with a special device made as a platform attached to polls. The platform could be rocked about the horizontal axis for 30 deg to both sides with the tether brought out of the pressure chamber.

To attain the stable pressure (i.e., pressure of saturated solution), the FEs were conditioned at the specified temperatures (80, 60, 40, 20, 0, -20, -40, -60 °C), and the temperature decreased from 100 °C to -60 "C). To attain increased temporary pressure (i.e., pressure of unsaturated solution), the FEs were conditioned at the specified temperature until the stable pressure was attained, and then the FEs were heated to a higher temperature.

RESULTS OF THE RESEARCH

Table 2 gives the parameters of FEs charging with Halon 121I-air and Halon 1211-nitrogen mixtures. In addition, two 8-liter FEs were also charged with Halon 1211-air and Halon 1211-nitrogen mixtures with the same parameters of liquid and gas charge density.

Table 2.

Fire Extinguisher Type	Type 1-2 liters	Type 2-3 liters
Capacity, l	2.29	3.155
Halon mass, kg	2.729	3.355
kV	0.65	0.58
Gas	air	nitrogen
Gas mass, kg	0.1465	0.1998
Charge density of Halon 1211, kg/l	1.192	1.068
Charge density of gas, kg/l	0.064	0.0633

The results of measuring pressure in the FEs during their stay in the thermal chamber at 80 °C and 60 °C depending on their preceding temperatures, are given in Figures 1-4 (the vertical straight lines, directed downwards, mean a pressure drop in the FEs as a result of their rocking

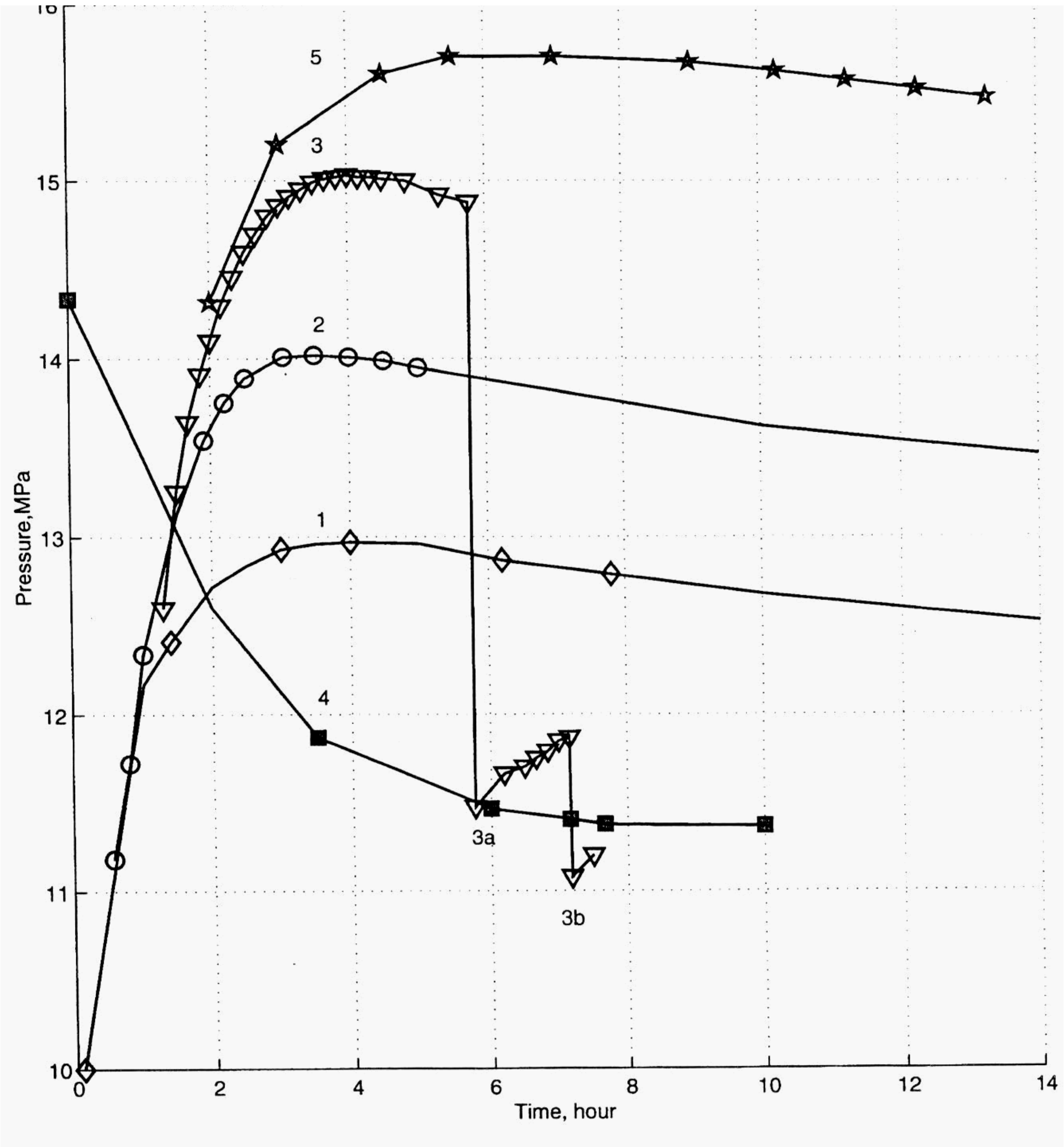

Figure 1. Pressure in 2-liters Type 1 fire extinguisher is plotted against the time of its stay in the thermal chamber at 80^0 C for various preceding temperatures: line ***1*** (diamonds) represents heating from 60^0 C to 80^0 C; line ***2*** (circles) represents heating from 20^0 C to 80^0 C; line 3 (triangles) represents heating from -60" C to 80^0 C; line ***4*** (squares) represents cooling from 100" C to 80^0 C. For comparison, line ***5*** (stars) represents pressure against the time of its stay for 8-liters Type 2 fire extinguisher heating from 20^0 C to 80^0 C; points a and b - shacking or rocking of the extinguisher. The charge of both extinguishers is Halon 1211 and air (see Table 2 for details).

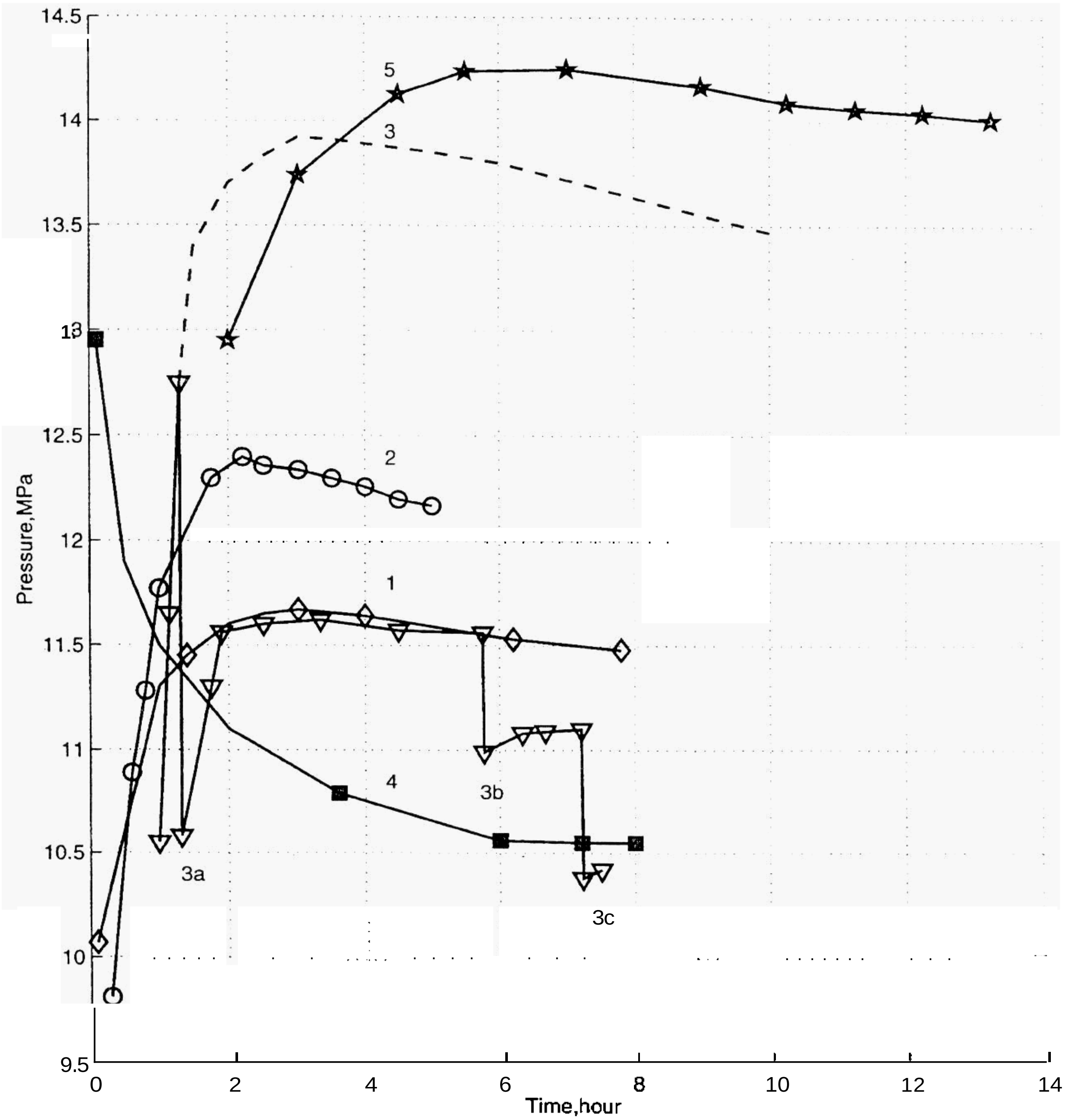

Figure 2. Pressure in 3-liters Type 1 fire extinguisher is plotted against the time of its stay in the thermal chamber at 80^0 C for various preceding temperatures: line ***1*** (diamonds) represents heating from 60^0 C to 80^0 C; line ***2*** (circles) represents heating from 20^0 C to 80^0 C; line **3** (triangles) represents heating from -60^0 C to 80^0 C, dashed line represents an extrapolation; line ***4*** (squares) represents cooling from 100^0 C to 80^0 C. For comparison, line ***5*** (stars) represents pressure against the time of its stay for 8-liters Type 2 fire extinguisher heating from 20^0 C to 80^0 C; points ***a*** and ***b*** - shacking or rocking of the extinguisher. The charge of both extinguishers is Halon 1211 and nitrogen (see Table **2** for details).

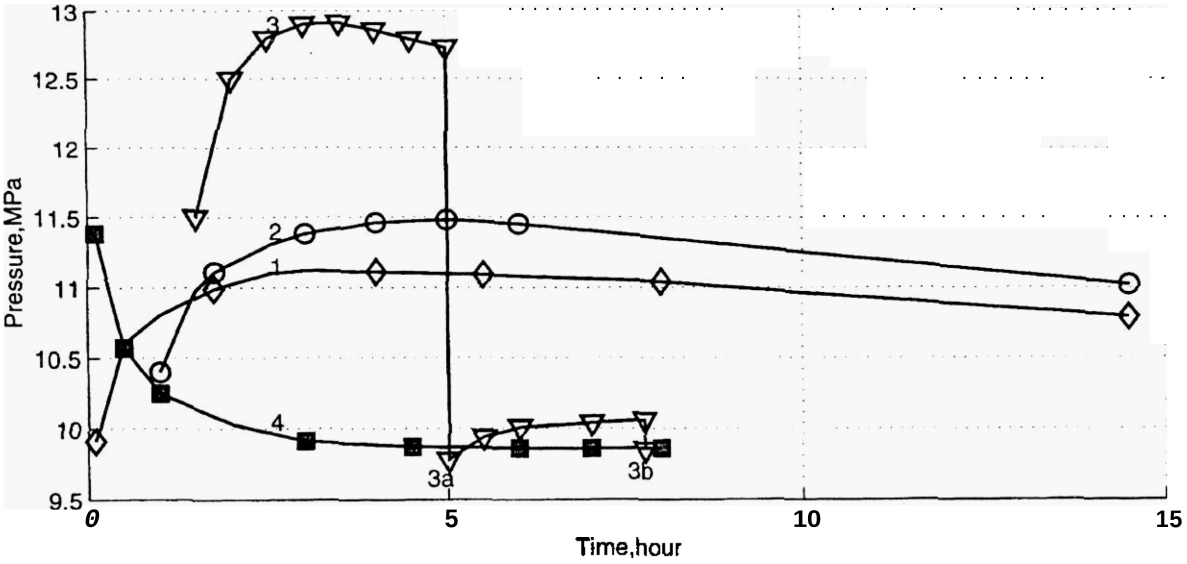

Figure 3. Pressure in 2-liters **Type** 1 fire extinguisher is plotted against the time of its stay in the thermal chamber at 60^0 C for various preceding temperatures: Line I (diamonds) represents heating from **40°** C to 60^0 C; line 2 (circles) represents heating from 20° C to 60^0 C; line 3 (triangles) represents heating from 0° C **to** 60° C line ***4*** (squares) represents cooling from 80^0 C to 60" C; points a and b - shacking or rocking of the extinguisher. The charge of extinguisher is Halon 1211 and air (see Table 2 for details).

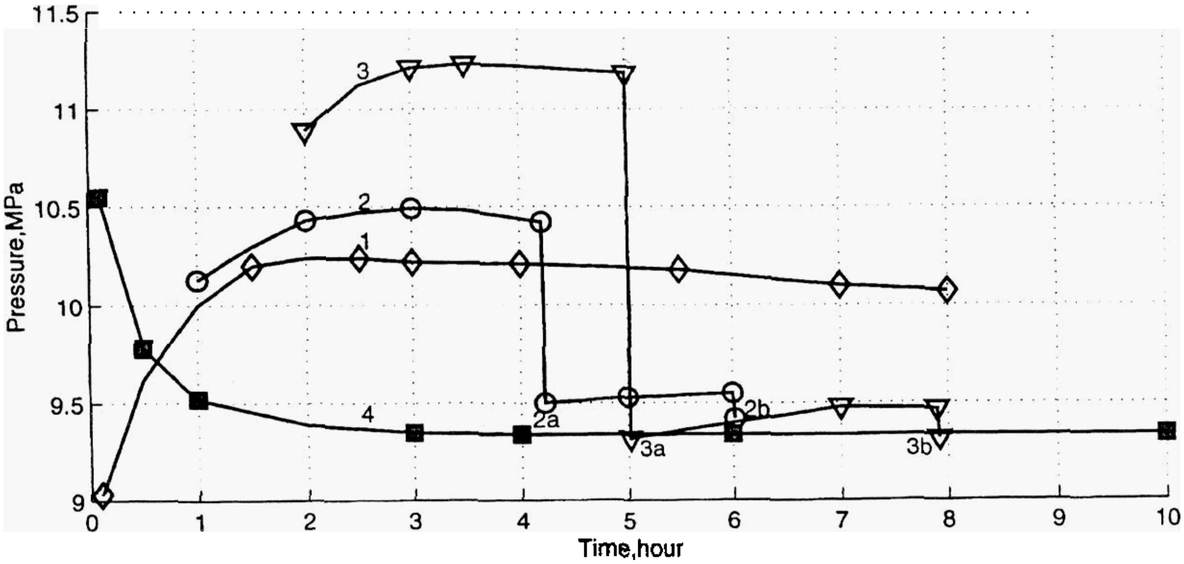

Figure 4. Pressure in 3-liter Type 1 fire extinguisher and with Halon 1211 and nitrogen extinguisher charge (see Figure 3 for details).

and shaking). The temperatures measured on the FE wall during its stay in the thermal chamber are given in Figure 5 (the temperature drops by 4-5 °C at the moment when the intensive gases dissolve in the liquid). Additional tests were run at the room temperature to evaluate the rate of air dissolving in Halons 1211,2402, and 1301 in FE rest and rocking conditions. Some results of the tests **at** 80 °C with different FEs and agents are tabulated in Table 3.

Table 3.

#	FE capacity, l	Halon	kV	Gas	Charge pressure at 20 °C, MPa	Pressure at 80 "C, MPa (min)	Pressure at 80 °C, MPa (max)	max/min (transient press. spike)
1	2	3	4	5	6	7	8	9
1	2	1211	0.65	air	8.2	10.7	15.1	1.41
2	3	1211	0.58	N_2	7.8	10.3	14.0	1.36
3	8	1211	0.65	air	8.2	10.7	15.7*	1.47
4	8	1211	0.58	N_2	7.5	10.3	14.3*	1.39
5	2	2402	0.66	air	9.3	11.6	15.5	1.34
6	8	2402	0.66	air	9.3	11.6	16.4	1.41
7	8	2402	0.684	air	9.3	12.7	18.9	1.49
8	2	1301	0.54	air	5.8	11.2	12.3	1.10
9	8	1301	0.605	air	5.8	12.2	14.7	1.20

* Preceding temperature is 20 °C, in other cases, it is -60 °C.

DISCUSSION OF THE RESULTS

As seen in Figures 1-4, variation of pressure in the FE put into the thermal chamber with a specified increased temperature, has a general character. The pressure rises quickly at first, then its rise rate gradually slows and the pressure reaches its maximum value, after this the pressure slowly falls. One can see that the maximum pressure value, its rate of rise and fall, depend on the FE preceding tempera-ture. The more it is away from the heating temperature, the higher is the maximum pressure, and the difference in pressures is rather considerable. For example, Figure 1 shows that with heating from 60 °C to 80 °C, the maximum pressure is 13 MPa; with heating from 20 °C, the pressure rises to 14 MPa, and with heating from -60 °C, the pressure has reached a value beyond 15 MPa. An even more striking difference was registered after an 8-hr cooling from 100 "C, when the pressure dropped to almost 11 MPa.

In reflecting on the pressure level for this air/halon mixture at 80 "C, what value is true? Apparently each value is true, but it depends on the way the temperature was reached and the time of its registration. With cooling from 100 to 80 "C, the equilibrium pressure is reached in 6-10 hrs; however with heating from 80 to 100°C, this pressure may be reached in several days. In particular, the FEs charged with Halon 1211 and kept at rest have reached the equilibrium state in 4-6 days, the FEs charged with Halon 1301 in 1-2 days, and the FEs charged with Halon 2402 in 6-8 days. This limiting pressure of saturated solution can be quickly reached by FE shaking or rocking. In this case, the pressure drops to a certain value comparatively quickly (in 1-2 min), and after this, the pressure drop stops and is confirmed by the vertical lines in Figures 1-4. And, as Figure **5** shows, bottle wall temperature decreases by several degrees, sometimes by 5 °C, which is why it rises again a little bit with further heating. With periodic shaking or rocking and further heating, the FE pressure and temperature stabilize; this means that the equilibrium state

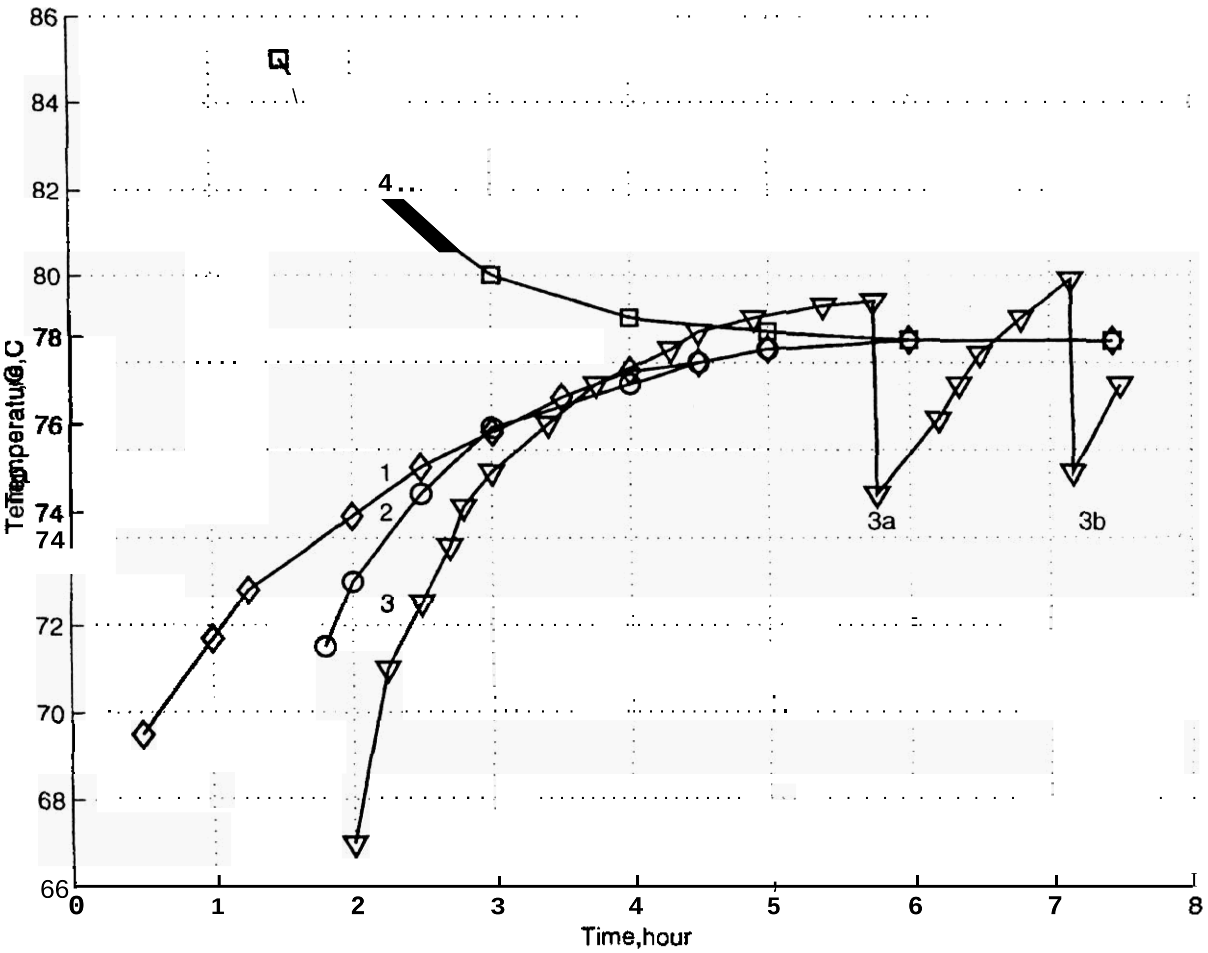

Figure 5. Temperature on the wall of 2-Liters Type 1 fire extinguisher is plotted against the time of its stay in the thermal chamber at 80' *C* for various preceding temperatures: line *I* (diamonds) - heating from 60^0 C to 80' C; line ***2*** (circles) - heating from 20' *C* to 80^0 C; line **3** (triangles) - heating from ***-60'*** C to 80^0 C; line ***4*** (squares) cooling from 100^0 C to 80^0 C; ***a, b*** - shacking and rocking.

between the gaseous and liquid phases has been reached or, in other words, we obtained the saturated gas-liquid solution. Additional measurements showed that the pressure stabilized after 100-140 cycles of rocking, in 1.5-2 min.

So, we can state that the halon and air (or nitrogen) mixture in the equilibrium state at the specified temperature has the minimum pressure value, and any increased pressure of the mixture is a temporary phenomenon that corresponds to the unsaturated solution. The level of solution unsaturation depends on the preceding temperature, temperature variation rate, FE size and form, and mixture composition. Figures 1 and 2 show that with the same charge parameters and the same preceding temperature (20 °C in this case), the temporary overpressure spike in 8-liter FEs with cylindrical bottles is approximately **1.5-2** MPa higher than that in 2-liter and 3-liter FEs with a spherical bottle. Apparently, this is associated not only with FE values but also with the relation between the liquid column height and table area. Comparison of the curves in Figures

1-4 shows also that the FEs more fully charged (with a higher kV value) with halon have a higher temporary overpressure spike.

A qualitative description of dissolved gas escape from a liquid is interesting for understanding a process of gas dissolving in a liquid. Ya. E. Geguzin in his book “Bubbles” studies two mechanisms (bubble and diffusive) of gas escape from an open bottle of aerated water [7]:

> At the beginning, the gas bubbles escape from the liquid quickly and actively, the liquid seethes and fizzes (bubbles are bursting at the liquid surface). Then the process slows down, the liquid settles down, i.e., ‘the bubble mechanism has exhausted or almost has exhausted itself, and the escaping gas can make use only of the diffusive mechanism. By simple calculations, one can see that it will take about a year for the gas to escape from the bottle by diffusion. But if we shake the bottle with aerated water which has settled down (i.e., we make water breaks and cracks which can be bubbles’ centers), the bubble mechanism should arouse - the settled down water, which is being poured into a glass, forms fizzing bubbles, i.e., when falling into the glass, water breaks in the same way as during shaking’. It can be assumed by analogy that when we shake and rock the FEs, the gas bubbles are captured by the liquid and gas dissolving (not degassing!) comes about much quicker than in the rest condition (approximately by 103-104 times).

D. **S.** Tsiklis [8] points to a very low rate of diffusive mechanism: “One should not have any doubts about the necessity of mixing since, as experiments have shown, the equilibrium cannot be attained only by diffusion even during many days.” Apparently, the angle of fall for the right branches of the curves in Figures 1-4, i.e., FE pressure drop rate, is determined by diffusive mechanism rate of air or nitrogen dissolving in halon (pressure drop rate was in the range of 0.3-1.5 MPa/hr). The form of the curves’ left branches is determined by the rates of thermal physics processes pertaining to the heating of the gas-liquid mixture: pressure rise of saturated halon vapors, increase of liquid volume due to decrease of its density, air or nitrogen pressure increase due to decrease of its density and free space. The maximum pressure is attained when these rates become equal.

When the FEs are cooled down, the pressure of saturated halon vapors decreases, the liquid contracts, the air or nitrogen pressure decreases due to an increase of its density and free space. As a result of this, the gas escapes from the solution and this phenomenon slightly slows the final rate of pressure decrease. When all the mixture acquires the temperature of the thermal chamber, a slow process of diffusive air escaping shall lead to a slight pressure rise, but we have not observed this during our 8-hour experiments. Apparently, the rate of gas absorption since in dissolving, the gas permeates into the solution by breaking downwards the boundary between the liquid and gaseous phases, and in gas escaping, breaking the boundary upwards is facilitated with hydrodynamic lift.

The following fact is of interest: to attain the equilibrium pressure when heating FEs, a portion of gas shall dissolve in the liquid Halon, i.e., the quantity of dissolved gas in the FE increases with the temperature rise, although there is a well-known method of degassing liquids by heating but admittedly under constant pressure. Further air or nitrogen dissolving during heating is corroborated by the results of calculations performed as per methods [9}. The further dissolving explains the cause of the fact that the FE pressure rises with increase of the difference between the preceding temperature and heating temperature. The lower the temperature, the more air or nitrogen is in the gaseous phase, and the higher the pressure is created by the gas during its heating in the time which lasts until it fully dissolves in the liquid.

This circumstance was probably a psychological barrier in some tests. In charging, the FEs were shaken and rocked, and in heating they were put at rest with a belief that the gas escapes from halon and is not absorbed during dissolving. This assumption has resulted in wrong methods and results (heating during a specified time period made it possible to obtain some intermediate values of unequilibrium mixture pressures), and discrepancies in results obtained during heating and cooling were taken for measurement errors. **We** can assume that the pressure was defined incorrectly in the higher temperature tests, which resulted in incorrect calculations for coefficients of gas solubility in liquids. The 1.5-fold and 2-fold difference in coefficients of solubility of different authors can be explained not only by methodological and computational causes but also by experimental causes.

CONCLUSION

By the results of experimental research it has been established that the pressure in the FE with the gas-liquid mixture depends not only on the charge composition but also on the conditions for reaching the specified temperature. The minimum pressure is attained when the equilibrium between the liquid and gaseous phases is reached, i.e., when the saturated solution is formed. This value is fundamental for this solution. It shall be defined throughout the whole operation temperature range and can be used to determine the coefficient of solubility. The saturated solution can be attained in the rest state (for several days) by cooling the FE down to a specified temperature (for several hours), when disturbing the FE state of rest by shaking and rocking (for several minutes). In the last case it is necessary to remember about the possible cooling of the mixture by several degrees. It is assumed that at rest the gas dissolving in the liquid proceeds by the diffusive mechanism, and in shaking and rocking it proceeds by the bubble mechanism.

It has been established by the experiments that as a result of the quick heating of the FEs, unsaturated solutions having various levels of unsaturation are formed, which results in substantial transient overpressure spikes (up to 150%relative to the unsaturated solution pressure). This value must be used for development of FE charge norms with due regard for FE operation characteristics. The in-flight cooling of aircraft fire extinguishing systems or aircraft parking in low temperature conditions (which is characteristic of some Russian regions) with further quick heating (e.g., with a hot air flow coming from an engine heater) are real situations simulated by our tests.

It has been established that a value of the maximum transient overpressure spike at a specified temperature depends on (1) the preceding temperature (the bigger the temperature difference, the higher the pressure is; (2) the degree of FE filling with halon (the more halon, the higher the pressure is; **(3)** the FE sizes (the bigger the FE, the higher the pressure is; (4) halon type (the higher the halon density, the higher the pressure is; and (5) gas type (the higher the gas solubility, the higher the pressure is; a coefficient of air solubility in Halons is higher than that of nitrogen).

The difference in time to attain the saturated solution at rest during heating and cooling can be explained by the fact that gas permeability into a solution (absorption during heating) is associated with breaking downwards the boundary between the liquid and gaseous phases, and gas escaping from a solution (degassing during cooling) is associated with breaking the boundary upwards, which is, apparently, facilitated with hydrodynamic lift.

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