NEW FIRE EXTINGUISHING AGENTS IN RUSSIA IN THE 1990s

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The resolutions of the Montreal Protocol have diminished halon manufacturing since the late 1980s with gradual production decrease before the year 2000, and the subsequent amendments to the Protocol imposed still more rigid time limits on halon manufacturing with final shutdown on 1 January 1994. Naturally, overall research activities for improved means and methods of ozone-friendly fire extinguishing have considerably increased since the end of the 1980s.

The original list of halons in the Montreal protocol included three popular fire extinguishing agents: Halon 2402, Halon 1211, and Halon 1301, the relative ozone-destruction potential (ODP) values of which are 6, **3,** and 10, respectively. Research of several dozens of bromine-containing halohydrocarbons showed that substitution of an atom of hydrogen for a chlorine or fluorine atom in a molecule of a fully substituted halohydrocarbon like the above halons, resulted in decreasing ODP value 10 times and more, practically without affecting the fire extinguishing capability of the agent.

As a result of joint research at the Russian Research Center "Applied Chemistry" Halon 1201, CF_2HBr, was developed; it was tested in the laboratory and full-scale fire test facility at "RD&PE Zvezda" Joint-stock Company (E.G. Belevtsev, G.Ya. Dricker et al., USSR authors' certificates Nos. 1755822 and 1761163 for Halon 1201 with small addition of Halons 1301 and 1211, priority granted April 26, 1990). Almost simultaneously, on May 17, 1990, this substance was presented by the Great Lakes Chemical Corporation, USA, under the trademark FM-100 (Firemaster). The ODP value of Halon 1201 was estimated in various laboratories (in Russia, at the Institute of Applied Physics and Chemistry of the Russian Academy of Sciences) to be in the range between 1.25 and 0.5 depending on the technique used and substance purity. In connection with information received from the Great Britain researches, the study was performed at the Institute of Genetics (Moscow), which showed that Halon 1201 had a mutagenous effect over Salmonella type bacteria. However, this conclusion cannot be applied to warm-blooded animals and humans; a similar conclusion was soon confirmed by American researchers.

Another fire extinguishing agent of the brominefluorohydrocarbons class with a low hazardous effect over ozone was Halon 2401, C_2F_4HBr, developed by ICI (Imperial Chemical Industries, UK), while in Russia it was manufactured at the RSC "Applied Chemistry" and tested at "RD&PE Zvezda." To compare fire extinguishing efficiency (FEE) and main properties of the currently used halons and new halons called as "first generation alternatives." see Table 1.

Among the halons, which were previously known but had limited applications, there is Halon 2202 (CF_2Br_2), which also shows the low ODP value (0.3) and high FEE (240 g/m^3). The results of halons' FEE evaluation have been obtained at a modified vertical glass Coward-Jones tube (G. Ya. Dricker, A.M. Ryvkin, S.A. Sukhov, USSR authors' certificate No. 1 173435). The pressure and the temperature in this tube can be controlled in the range from the vacuum to the environmental conditions and from the room temperature to 200 °C, correspondingly. The air-fuel-inhibitor mixture prepared beforehand have been ignited using a torch-like flame with the air-tight shutter between the tube and tube prechamber open.

TABLE I. COMPARATIVE PROPERTIES OF THE CURRENT AND NEW FLRE EXTINGUISHING HALONS.

No.	Halon	Chemical formula	FEE for TC-I (aviation fuel) vol% (reduced to 20 "C)	FEE for TC-I (aviation fuel) g/m^3 (reduced to 760 nini Hg)	M. g/mol	Boiling temperature, °C	Density, g/cm^3	ODP
I	2402	$C_2F_4Br_2$	2,5	270	260	47	2,18	6
2	1211	CF_2ClBr	3,6	250	I65	- 4	1,83	3
3	1301	CF_3Br	4,2	260	149	- 57	1,57	10
4	1201	CF_2HBr	4.4	240	131	- 15	1,85	0,6
5	2401	C_2F_4HBr	3,7	270	181	3,7	1,81	0,3

The iodine fluorohydrocarbons are also among the efficient fire extinguishing agents. but they have not found their application yet due to their physical and toxicological properties. In Russia, attempts are being made to make use of the iodine-containing hydrocarbons' positive features by their dilution with fluorine-containing hydrocarbons. These efforts by A.N. Baratov, A.F. Zhevlakov and E.V. Tiinofejev (VNIIPO, All-Russia Research Institute of Fire Defense, Proceedings of Conference, Part 1, Moscow, 1999, pp. 259-260) result in ozone-friendly combined compositions with FEE as that of Halons 2402 and 1301 owing to the effect of synergism.

The systematization of results obtained in various experimental studies and methods for physical and chemical property analysis has made it possible to compile a large database for brominehalohydrocarbons (halons). The present author took part in the Soviet-American Conference on Halons (Leningrad, May 1991) where he presented a paper "Determination of bromine-containing Halon properties with the purpose to search for ecology-friendly fire extinguishing agents." The paper presented methods to analyze all properties necessary for halon applicability evaluation: fire extinguishing concentration (9% precision), boiling temperature (1 %), liquid density (2%), critical temperature (0,8%), critical pressure (8%), critical volume (4%), and toxicity (maximum allowable concentration, 40%). The paper showed that it is sufficient to know a chemical formula of a substance to analyze its properties.

Constructing or finding a molecule with desired properties makes it possible to meet the contradictory requirements to fire extinguishing substances (high FEE, high liquid density, fair evaporation rate. low toxicity, low ODP). While analyzing the database compiled of test results and analyses, quite a number of bromine-containing halons were found, whose physical, chemical, and fire extinguishing properties were not inferior or even superior to those presently in use, but with lower ODP value (i.e., meeting the ODP≤ 0.2 requirement according to the US Clear Air Act Amendment, 1990). As an example, take Halons 1102 ($CFHBr_2$) and 2302 ($C_2HF_3Br_2$) (**J.S.** Nimitz, S.R. Skaggs, and R.E. Tapscott "Next-Generation High-Efficiency Halon Alternatives." *Proceedings*, International CFC and Halon Alternatives Conference, Baltimore, MD. pp. 632-641, 1991). Evidently, the presence of atomic bromine in the molecule (the principal element in the mechanism of chemical flame inhibition) does not yield zero ODP value, though application of new bromine-containing halons would considerably (10–20 and more times) decrease the hazardous effect over atmospheric ozone without any loss of fire extinguishing system efficiency.

However, the Copenhagen meeting of the Montreal Protocol member states in November 1992 imposed a complete ban on manufacturing of transition bromine-containing halons since January 1, 1996, but at the same time granted a quota for manufacturing of these Halons for crucial applications. Thus, the Copenhagen Adjustments, in an attempt to improve the ecological situation, in fact resulted in its deterioration as they render useless any further research of new highly efficient low-toxic bromine compounds with desired properties; in other words, they legalized conservation of the actual scientific and technological level in this field of knowledge.

The situation is especially painful in Russia where the leaders of respective industries, transportation and other economic sectors, have no command of up-to-date and comprehensive information on international resolutions, including those ratified by the Russian party. Taking into consideration the economic reform that is underway in Russia and the fact that Russia, different from industrially developed countries, has no stock of halons (USA, for instance, possesses a 40-year supply), the situation is really grave, especially if one considers direct and indirect damage inflicted by unextinguished fires. And as a consequence of these bans when similar drop-in halons have not been found yet, the solution of the fire safety problems in especially important areas is associated with great, sometimes insurmountable, difficulties. For example, the Russian fire extinguishing systems for civil and military aviation are primarily based on Halons 2402 and 1211. And if the Halon 2402 problem acuteness is somewhat smoothed over owing to its earlier production of large quantities, which are being withdrawn from other areas where its application is not necessary, and supplied to vital areas after regeneration, currently there is no reasonable solution for the painful problem of Halon 1211 supply and adequate replacement.

Thus, the world community is still unable to find an adequate substitute with a zero ODP value for halons. Therefore, at present suggestions are made to use low-efficiency mixtures as fire extinguishing agents, that do not affect the ozone layer, for instance, neutral gases. To dilute the fire atmosphere with nitrogen, V.N. Marshakov and G.V. Melik-Gaikasov (Institute of Chemical Physics of the Russian Academy of Sciences, Patent 2069064), have used ammonium azide tablets pressed to the density of 1.31–1.32 g/cm^3 and coated with a polymerous lacquer for protection. The part of nitrogen in the tablet is 93.3 %, i.e., its density is 1.22 g/cm^3 whereas the liquid nitrogen density is 0.8 g/cm^3, and the gaseous nitrogen density at 15 MPa pressure and 20 °C is 0.17 g/cm^3. To decrease atmospheric toxicity and to ensure environmental protection, M.N. Vaisman and **S.S.** Pustynnikov (VNIIPO) suggest a gas mixture of 10–30% of SF_6 gas and 70–90% of nitrogen (authors' certificate No. 1701328).

Carbon dioxide is finding increasingly wide application, despite the hothouse effect it produces. S.N. Osipov (Belorussia Polytechnic Institute) suggests extinguishing fire sources with a saturated carbon dioxide water solution (authors' certificate No. 1806795). In fire extinguishing systems for computer rooms, gaseous argon is supposed to be applied. This has much in common with Inergen, a mixture of nitrogen, argon, and carbon dioxide, vigorously promoted in the West. For example, at the conference on the problem of halon replacement, held in St. Petersburg, September 1999), Andrew Kim (Canada) (told about large-scale fire tests with argon and Inergen as halocarbons alternatives, which, in their turn, fall within the limiting action of the Kyoto Protocol on the substances with the GWP (Global Warming Potential).

This group of chemical compositions (fluorocarbons and fluorohydrocarbons) are being extensively studied as the main alternatives for fire extinguishing halons. While the effect of inert gases over flame is purely physical (dilution and heat removal), the fluorine compounds have little chemical effect, which is much less than that of bromine compounds. While choosing fluorine compounds, it should be known that some are combustible (CH_2F_2, CH_3F, $C_2H_3F_3$, $C_2H_4F_2$) or difficult combustible (C_4F_8), and some show a high GWP (CHF_3, C_4F_{10}, C_5F_{12}). At present, the All-Russia Research lnstitute of Fire Defense (VNIIPO MVD RF) has issued the official fire safety norms for gas fire extinguishing systems, which include C_2HF_5, CHF_3, C_4F_8, C_4F_{10}, and C_3HF_7. These substances have low boiling temperature and FEE 2–2.5 times lower than that displayed by halons, they are nontoxic and can be used in the pi-esence of humans. Fluorine compounds are 2–3 times as expensive as halons. They can he applied in areas where fire extinguisher mass and dimensions are irrelevant. In aviation and in other applications where mass and dimensions of fire extinguishers are crucial. the application of fluorocarbons is hardly practicable: low liquid density (1.13 kg/l at 20 °C, C_2HF_5) and low efficiency (450 g/m^3) would require four C_2HF_5 fire extinguishers instead of one using Halon 2402.

Taking into account the raw material resources available in this country and technological capabilities of production facilities, experts from the Urals "Galogen" Manufacturing Association are inclined to accept mass-scale production of chlorine-containing fluorohydrocarbons C_3HF_6Cl and CHF_2Cl, though their ODP values are above zero (0.02–0.04). Chlorine slightly improves the agent efficiency, but still the replacement of one fire extinguisher with Halon 2402 would require three with CHF_2Cl.

Famous foreign specialists contribute to development of new fire extinguishing agents in Russia. For example, M. Robin and U. Iicubo (GLCC, USA), have patented in Russia (Patent 2068718) fluorohydrocarbon compositions C_2HF_5, C_3HF_7, $C_3H_2F_6$ in the mixture with Halons 1301, 1211, 2402, 1201 and 2402. R. Grin (Canada) has received Patent 2079318 fora fire extinguishing mixture of the first of group substances. which includes $CFCl_3$, $C_2H_2F_2Cl_2$, $C_2HF_3Cl_2$, and the second group substances. which includes terpadienes (30 compositions) and unsaturated oils (12 compositions and their mixtures). A substance may also include $CHFCl_2$, $C_2F_4Cl_2$, CHF_2Cl, C_2HF_4Cl, C_2HF_5, $C_2H_2F_4$ or their mixtures. These fire extinguishing mixtures with the trademark **NAF** (e.g., 90% $CFCl_3$ and 10% linoleic acid) have ODP=0.9.

Traditional research of fire extinguishing water solutions continues. **A** team of inventors from the State Research Institute of Chemistry (GosNiiKhimia) has proposed a urea (20–40%) and melamine-urea-formaldehyde resin (20–50%) water solution, a nontoxic fire extinguishing composition producing solid byproducts. Inventors from the town of Stakhanov (G.Yu. Valukonis, M.G. Levertov. and others) suggest potassium- and magnesium-containing water solutions of the mineral bischofite (authors' certificate No. 1787458), water bubbling of bromine chloride resulting in the production of crystalline hydrate $BrCl*3H_2O$ (authors' certificate No. 1673141), use of titanium production waste matter—the melts ofpotassium. magnesium, manganese, titanium, chromium, and iron salts (authors' certificate No. 1792719). S.A. Kurov, N.M. Kravets, and others (authors' certificate No. 1643022) suggest to mix caustic and chlorine production wastes (water solutions of salts) with hydrophilic high-dispersion silicon dioxide.

As a substitute for toxic and corrosive ethyleneglycole, which is often used in low-freezing water solutions. a water solution of potassium acetate was developed (V.P. Barannik, G.Ya. Dricker, and others, authors' certificate No. 1725928), which is efficient in extinguishing not only smoldering but also open flames of liquid fuels and solid materials. It is ecology-friendly, nontoxic, and noncorrosive for steel and aluminum alloys, and tin-lead solder, which makes it usable to temperatures as low as -45 °C. B.V. Kononov and Z.P. Puck (Enterprise "Soyuz," Patent 2050866) apply to the fire atomized water under the pressure of 0.5–5 MPa with intensity of 10–300 m/s. This water is saturated up to ultimate solubility with a salt which inhibits combustion. Then a fire extinguishing aerosol is supplied to the fire area in the quantity of 0.005–0.01% of the solution mass. A.I. Gurov et al. (Moscow Aviation Technology Institute named after K.E. Tsiolkovsky) suggest mineral–water suspension, which consists of liquid glass (7–16 mass%), clay (13–72 mass%) and water (20–80 mass%) (Patent 2098158).

New foamers are being developed. V.M. Moiseenko and M.V. Odinets (authors' certificate No. 1690795) suggest adding polyvinylpirrolidone to the aqueous solution of a fluorine organic substance and primary alkylsulphate salts. M.V. Puzano, M.N. Vaisman, and M.V. Nazarov (authors' certificate No. 1641369) introduce ethylene glycol as a solvent, and dimethylphormaldehyde as a stabilizing agent in a composition containing surface-active substances and Halon 2402. A foamer composition based on secondary alkylsulphates C_6-C_{16}, chromatocyclohexilamine and fluorine organic additive, has been suggested by V.M. Kucher, V.M. Gida, V.A. Merkulov, and others (authors' certificate No. 1701329). For application in the Northern latitudes, Kh.A. Gaisumov (Patent 2022588) suggests a foam stabilizer, which includes ammonium hydroxide or ammonium chloride (**6–12** mass%) and calcium chloride (12–21 mass%); the rest is water. N.N. Dykhanov and others (Patent 21 10307) suggest a foaming composition (mass%): natrium alkyl sulphates 16–21, urea 20–35, polyethyleneglicol with M=400-5000 0.16–0.21, urea chromate 0.04–0.06, and the rest is water.

Research on new fire extinguishing powders is also ongoing. G.Yu. Valukonis and co-authors (authors' certificates Nos. 1692598 and 1819642???) suggest producing a fire extinguishing powder by mixing urea with halogen derivatives of non-branched saturated hydrocarbons, and to increasing powder efficiency by dispersing the basic component or part of it up to the dispersion degree of 10^6–10^8 1/cm. V.A. Levitskii and co-workers (authors' certificate No. 1797923) suggest decreasing powder caking by applying a white soot with specific surface above 100 m^2/g, dried at 100 °C to 0.1–0.5 mass percent of moisture content. M.N. Vaisman, A.V. Dolgovidov, and M.V. Kasakov (VNIIPO) add azodicarbonamide (3–20%) to the fire extinguishing powder (authors' certificate No. 1729529), and the third component is n-toluene sulphonic acid (S.N. Buyev, M.N. Vaisman, Patent 2077121). V.I. Uldyakov and G.Yu. Stepanova (Patent 21 10306) add aerosil (0.5–3%) and alumina (7–10%) to ammophos. To improve fire extinguishing powder efficiency by 1.15–1.5 times, S.B. Dornostoop, V.A. Vasilchenko, **A.E.** Egel (Orenburg Polytechnic Institute) and A.N. Baratov (VNIIF'O) treat a non-organic salt in the electrostatic high-voltage field of 500-1000 V after grinding it.

Some of the inventions relate to powders for metal fire extinguishment. S.G. Gabrielyan, N.P. Kopylov, and others (EcoKhimMash) present powder compositions for aluminum-organic compound fire extinguishment (Patents 2108125 and 2108 126): potassium chloride, plumbago, anticaking additive, perlit and aminoplast. In another invention (Patent 2088290) the composition also includes phenylon, silicium dioxide and calcium carbonate. A.E. Kurepin and others (Machine-Building Research Institute, Patent 21 19368) suppress alkaline metal and alkaline earth metal fires with melamine cyanurate (10-60%) and high-temperature additives: ammonium, magnesium, and titanium oxides.

Zhartovsky and others (Patent 2027455) have developed **a** multipurpose fire extinguishing powder, which includes hydrophobic aerosil (0.3215%), hydrophobized ammonium sulfate (10–50%), and the rest is hydrophobized monoammonium phosphate: in Patent 2086279, the components are ammophos (35–45%) with the particle size of <50 μm, silicium dioxide (0.526%), ammonium sulfate (35–45%), and the rest are aluminum silicates. **A.S.** Choomuck and others present a fire extinguishing powder, which consists of aerosil (0.5–2%), dried spent sulphuric acid solution for the wire rod pickling (25–55%) and the rest are the wastes of ammonium chlorate production. Kolosov and others (Institute of Polymeric Materials. Patents 20.50876 and 207 1798) add 0.2–0.5% of alkylhaloidesilane liquid *to* potassium chloride in order to hydrophobize and improve powder composition fluidity.

Operational and technological drawbacks of fire extinguishing powders (tendency for moisture absorption, caking and granulation, heterogeneous composition at mechanical production) limit the range of their application. Attempts have been made to avoid these problems by applying the pyrotechnical method of highly dispersed solid particles production, which gives a means of volumetric fire extinguishing, namely, gas and aerosol producing compositions of the self-activating extinguishing type (SEC). **A** group of authors (M.N. Vaisman, Dolgovidov, and others, authors' certificate No. 1725929) suggested a powder composition (80–97%) with solid nitrodicarbonamide fuel (3–20%), which gives off a gas/aerosol mixture into the protected volume under the influence of high temperature or a chemical reaction between the components. Various versions of inert gas, powder and gas/aerosol composition mixtures have been suggested in authors' certificates Nos. 1741815, 1741816, and 1741817 (M.N. Vaisman, V.I. Makejev, and others). According to these authors, substances with high chemical activity are produced in the process of fire extinguishing, and a gas/aerosol mixture in fire testing performs 3–5 times as effectively as halons. It has been found that each gram of SEC produces up to 0.4-0.6 liters of gas mixture (nitrogen and carbon dioxide) and up to 0.4–0.6 grams of highly dispersed solid particles, which size does not exceed 2–5 μm (up to 90%). The solid particles are composed of carbonates, bicarbonates, chlorides, oxides, and hydroxides of alkali metals.

A research team of "Soyuz" Research and Manufacturing Association (Lubertsy), "Tekhnolog" specialized design bureau and the Leningrad Technological Institute (named after Lensoviet) patented (No. 2001647) a fire extinguishing composition, which consists of epoxy resin (10–14.5%), potassium perchlorate (2–2.5%), **isomethyltetrahydrophthalanhydride** (12–15%), carbon or dyer (0.001–0.5%), sulphoricinite (0.01–0.5%), and the rest is potassium nitrate. In another patent issued to the same team of workers (No. 2001648), polyether resin (7.5–30%) was added.

Solid fuel compositions producing aerosols have been developed at the Perm plant (named after S.M. Kirov) (A.D. Sergijenko and others. Patents 2076761,2080137. 2107254). They are composed of polymeric binder based on rubbers or polyethers (15–20%), potassium nitrate (60–70%) and solid fuel with a combustion catalyst. To produce the aerosol producing composition, V.G. Schetinin (Patents 2050877 and 2050878) uses compounds consisting of potassium and substances with high cornbustion heat: aluminum, manganese, bromine, chroniates and horates. In Patent 2108 124, A.N. Baratov and others have proposed an aerosol based on the red phosphorus (20–25%). potassium nitrate (75–80%) and potassium phosphate (5–50%), which is produced by manual-press mixing of the components.

According to the research, SEC are low toxic, their corrosiveness is quite low. However, there are shortcomings: high temperature in a local area of the protected volume. undesirable effect produced by the gas/aerosol mixture over some electronic and optical equipment, decrease of visibility to 0 in the protected volume, and an unclear possibility of SEC use in the unsealed ventilated rooms and those of complex configuration.

An invention of a group of scientists of the Institute of Chemical Physics (V.V. Azatian, R.G. Aivazian, V.I. Kalachiov, and A.G. Merzhanov, Patent 2042366) looks rather original among other inventions. The authors suggest using alkane/alkene mixture with a number of carbon atoms in the molecule in the range of 1-6 (e.g., bottled domestic gas) as an inhibitor to prevent inflammation and explosion of the hydrogen/air mixtures.

A vast number of Russian inventions in the area of new **fire** extinguishing agents development have not been discussed in this paper.

The survey of inventions in Russia and other CIS countries since the Montreal Protocol on ozone layer protection shows that work has been under way in the search for novel fire extinguishing agents among new halons, inert gases, fluorochlorohydrocarbons, fluorohydrocarbons and fluorocarbons, water solutions and powder foamers, powders, and self-activating fire extinguishing compositions. These research and testing activities became possible owing both to the initiative and scientific interest of the authors and to state financing, though very low and insufficient. At present, the federal program on search of alternatives for the prohibited chloroflourohydrocarbons cannot catalyze research and development in various economic sectors. Now there are a few of specialists in flame inhibition and new fire extinguishing agents both at the VNIIPO (All-Russia Research Institute of Fire Defense) and other research centers. All these factors (the lack of halon stocks, brain drain, inadequate funds, and the lack of purpose-directed technical policies) would result in the necessity for Russia to purchase expensive imported fire extinguishing agents and, maybe, even fire extinguishing systems, the prospect of which is fraught with dangerous consequences in technological backwardness and lower living standards.

Funds that must be invested now will help earn hard currency returns tomorrow and contribute to the salvation of the country from the catastrophe of unextinguished fires, unsuppressed explosions, and human lives lost.