DuPont™ FM-200®

TECHNICAL PROGRESS

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Abstract

FM-200® (HFC-227ea; 1,1,1,2,3,3,3-heptafluoropropane) is a recently developed, zero ODP fire suppression agent designed for the replacement of Halon 1301 in total flooding fire suppression systems. Recent technical progress in the fire suppression applications of FM-200® are discussed, including total flooding applications, the solubilities of inert gases in FM-200®, and the suppression of hydrogen combustion by FM-200®.

Total flooding applications of FM-200®

Class A Hazards

The effectiveness of FM-200® on Class A fires has been investigated as part of the test requirements of Underwriters Laboratories and Factory Mutual for listing and approval of FM-200® fire suppression systems, and has also been investigated in detail by Hughes Associates, Inc.[1]

As part of the test requirements for listing and approval by Underwriters Laboratories and Factory Mutual, the extinguishment of wood crib fires was examined in a 1200 ft^3 enclosure.[2] These tests employed an 18"x18"x 6" wood crib, ignited with n-heptane and allowed a preburn of 5 to 6 minutes. Test requirements also included maintenance of oxygen above 20.0 %, and were conducted at an FM-200® concentration of 5.8%, rather than the design concentration of 7.0%. The pass/fail criteria for the test was that the fire be extinguished, that no reignition occur after removing the crib from the enclosure following a 30 minute soak period, and that no free burning embers be observed. The test has been successfully completed at an FM-200® concentration of 5.8 % by a number of original equipment manufacturers (OEMs) as part of their listing/approval test requirements.

The Hughes Associates, Inc. study[1] examined the effectiveness of FM-200® on Class A fuels including printed circuit boards, PVC-coated wire bundles, magnetic tapes and shredded paper. One of the major objectives of this study was to determine the levels of HF produced from FM-200® following the extinguishment of realistic fires which might be expected to occur in an electronic data processing (EDP) facility. As a result, it was desired to produce test fires of a realistic size, taking into consideration the sensitivity of modern detection systems. The test enclosure consisted of a 2562 ft^3 volume equipped with an ionization detector located 14 feet from the fuel source, representing a worst case with a 20 foot on center detector spacing. Delay times of 10 and 30 seconds following detection were employed before discharge of the suppression system. HF concentrations were measured via an in situ infrared absorption technique, employing a Fourier Transform infrared (FTIR) spectrometer. The test fuels included shredded paper, PC boards, PVC coated wire cables, and magnetic tape, representing the most common fuel sources expected to burn in a computer room environment. All fires were extinguished with the minimum design concentration of 7% FM-200®.

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For all Class A fuels examined in this study, FTIR analysis indicated that carbonyl fluoride was not present in the post-extinguishment atmosphere.

For a 10 second discharge of FM-200®, extinguishment of PC board fires produced HF concentrations ranging from 9 to 31 ppm HF, and extinguishment of shredded paper fires produced HF concentrations in the range of 48 to 175 ppm. For a 10 second discharge of FM-200® extinguishment of PVC cable fires produced HF concentrations ranging from 37 to 58 ppm. For comparison, joint industry studies[3,4] conducted by DuPont, Fenwal, Cardox and Ansul reported that PVC fires extinguished with 5% Halon 1301 produced a maximum HF concentration of 37 ppm; HBr concentrations were not reported due to HCl interfering with the analysis, but were likely of the same order of magnitude as the HF concentration. Hence, the total decomposition products (TDP) are of approximately the same order of magnitude in the two studies. Fires of closely packed spools of magnetic tape extinguished with FM-200® produced HF concentrations ranging from 56 to 89 ppm HF. For comparison, the joint industry studies[3,4] conducted by DuPont, Fenwal, Cardox and Ansul reported that magnetic tape fires extinguished with 4% Halon 1301 produced maximum HF and HBr concentrations of 52 and 62 ppm, respectively. Hence, the total decomposition products (TDP) are again of approximately the same magnitude in the two studies.

The Hughes Associates, Inc. study of Class A fire suppression with FM-200® described above can be regarded as a worse case scenario due to the high ceiling height and lengthy detection times employed, and also due to the small volume of the test enclosure. More rapid detection and larger enclosure volumes typical of actual computer and EDP facilities would be expected to result in HF concentrations lower than those observed under the test conditions. The study clearly demonstrates that HF concentrations can be reduced and controlled through proper engineering. In addition, it was observed that for Class A fires typical of those expected to be encountered in computer and EDP facilities, the amount of HF produced following extinguishment by FM-200® is of the same approximate magnitude as the total decomposition products (HF plus HBr) formed from Halon 1301.

Class B Hazards

The effectiveness of FM-200® on Class B hazards has been examined in laboratory[5], intermediate[6-11] and large-scale[12-15] investigations.

3M Company[9] reported the results of a study on the extinguishment of n-heptane pan fires ranging in size from 0.3 to 7.7 kW in a 45 ft^3 enclosure, with Halon 1301, FM-200® and CEA-410. For a given fire scenario, FM-200® and CEA-410 were observed to produce approximately the same amount of HF, which for the large fires was approximately 5-6 times the TDP produced from Halon 1301. For the smaller fires, the HF produced from CEA-410 or FM-200® was 2-3 times that produced from Halon 1301. In addition, it was noted that the HF concentration was reduced by a factor of two (i.e., halved) upon increasing the agent concentration from the cup burner value to the cup burner value plus 20%.

DiNenno, et. al.,[6,10] reported on the extinguishment of 0.3, 1.4 and 3.2 kW/m^3 n-heptane pan fires with FM-200® in a 42 ft^3 enclosure. Hydrogen bromide concentrations were not reported in this study. However, assuming that the concentration of HBr produced from Halon 1301 was of approximately the same magnitude as the HF produced, the HF produced following extinguishment of the test fires with FM-200® would be calculated to be approximately 2 to 4 times the TDP produced upon extinguishment with Halon 1301. Based upon small and intermediate scale test data developed at Hughes Associates, Inc., Hanauska, et. al.,[7] developed scaling factors to allow the estimation of HF production as a function of the fire size to enclosure volume ratio for Halon 1301 and its proposed replacements. Scaling factors for the HFCs and PFCs were similar, and greater (3-6 times) than the scaling factor for Halon 1301.

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Brockway[11] examined the extinguishment of 0.1 to 3.7 kW n-heptane pan fires in a 45 ft^3 enclosure with FE-13™, CEA-410 and FM-200® at the cup burner and higher extinguishing concentrations. Brockway observed that compared to the cup burner concentration plus 20%, no further decrease in the amount of decomposition products resulted from increasing the concentration to cup burner plus 40% or cup burner plus 60%, although the extinguishing time was observed to decrease slightly with increasing agent concentration.

Hansen, et. al.[14], reported the extinguishment of n-heptane and diesel fires in a 19,776 ft^3 machinery space. For a combination 500 kW n-heptane spray/500 kW n-heptane pool fire, 7% FM-200® produced 2000 ppm HF. Extinguishment with 6.0% CEA-410 produced 4500 ppm HF, and with 16.0% FE-13™ produced 1200 ppm HF. It should be noted that a higher concentration of FE-13™ than cup burner plus 20% was employed in these tests. Extinguishment of the same fire with 5% Halon 1301 produced 300 ppm HF. Hydrogen bromide concentrations were not reported in this study. However, assuming that the concentration of HBr produced from Halon 1301 was of approximately the same magnitude as the HF produced, the HF produced following extinguishment of the test fires with FM-200® would be calculated to be approximately 2 to 3 times the TDP produced upon extinguishment with Halon 1301. Extinguishment of a combination 2 MW n-heptane spray/500 kW n-heptane pan fire with 7% FM-200® produced 3500 ppm HF. Extinguishment of a combination 5 MW diesel pan fire/500 kW n-heptane spray fire/cable tray fire with 7% FM-200® produced 9000 ppm HF.

The studies cited above demonstrate that the amount of HF produced from the extinguishment of Class B fires with FM-200® is approximately two to six times the total decomposition products formed from extinguishment of the same fire with Halon 1301. Figure 1 summarizes the results of six independent studies of thermal decomposition product formation from FM-200®, including the suppression of both Class A and Class B fires. These studies employed FM-200® at a design concentration of between 7% and 8% by volume, and the average HF concentrations observed are shown in Figure 1. As can be seen from Figure 1, the agreement between the studies is excellent, and the concentration of HF produced following the extinguishment of Class A and Class B fires with FM-200® is observed to be a linear function of the fire size to room volume ratio. This correlation allows prediction of the amount of HF produced, given the fire size and room volume.

Solubility of inert gases in FM-200®

The solubility of inert gases in FM-200® was determined as previously described for the determination of the solubility of nitrogen in FM-200®[16]. The experimental apparatus consisted of a 300 mL DOT-3E-1800 stainless steel cylinder, fitted at both ends with a Whitey SS-16DKM4F4-1 Series D valve with rupture disc. An Omega PX-602-500GV pressure transducer was connected to one of the Whitey valves to allow monitoring of the pressure. The total volume of the apparatus was found to be 306 cm^3, determined by filling with water and weighing. Temperature control was accomplished by immersing the entire apparatus in a Neslab refrigeration unit, accurate to 0.1°C. The apparatus was tared, filled with the desired amount of high purity (99.9999 %) FM-200® and the weight of FM-200® determined by difference. The apparatus was then pressurized with the desired inert gas, and the amount of inert gas introduced determined by weighing the apparatus. The apparatus was then placed in the constant temperature bath and the pressure versus temperature data recorded. With vigorous, frequent agitation of the apparatus, equilibration was typically attained within 30 minutes.

The solubilities of nitrogen, air, argon, helium and carbon dioxide in liquid FM-200® were calculated from the experimental data via the method described by Yang, et. al.[17], and are summarized in Table 3, which shows the solubility constant (reciprocal of the Henry's Law coefficient) at 70°F. The observed order of solubility was $CO_2 >> Ar \approx air \approx N_2 \approx He$. Air is slightly more soluble than nitrogen, which is consistent with the expected higher solubility of O_2 compared to N_2 The solubilities of air, nitrogen, argon and helium in liquid FM-200® are all low and of the same magnitude, whereas the solubility of CO_2 in liquid FM-200® is higher by at least an order of magnitude.

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Yang, et. al.[18] have recently measured the mass of nitrogen required to superpressurize FM-200® to three different pressure levels at 73.4°F, for a fill density of 58.2 lb/ft^3. Table 4 compares the results of Yang to those calculated employing the nitrogen solubility measured previously by DuPont[16]. As can be seen from Table 4, the agreement between the two sources is excellent.

Suppression of hydrogen combustion

Hydrogen is an important industrial chemical in petroleum refining, in synthesis of methanol and ammonia, in the manufacture of various chemicals, and also finds use in metallurgical processing, vegetable-oil hydrogenation, electronics manufacture and fuel cell applications[19]. The danger in the use of hydrogen lies in its extreme flammability in oxygen or air. Hydrogen is odorless, colorless, and burns with an almost invisible flame. As a result, hydrogen is not readily detected, further increasing the danger of its use compared to other flammable substances. Detonation and flammability limits for hydrogen are wider than those of most other flammable gases. The difficulty of suppressing hydrogen combustion and fires is evident from the large quantities of Halons, in particular Halon 1301, required for suppression. Whereas a large selection of Class A and Class B fuels are sufficiently protected by a concentration of 5% by volume Halon 1301, suppression of hydrogen fires with Halon 1301 requires at least 20% by volume Halon 1301[20].

For the more than 50 fuels tested to date, FM-200® has been found to be less efficient compared to Halon 1301, on both a volume and weight basis. Surprisingly, we have found that FM-200® is superior to Halon 1301 in the extinction of hydrogen fires, on both a volume and weight basis. The concentrations of FM-200® and Halon 1301 required for the extinguishment of hydrogen diffusion flames were measured employing the laboratory cup burner apparatus. The apparatus consisted of a 12 mm OD Pyrex burner located inside a 102 mm ID Pyrex chimney; the linear velocities of air and fuel were matched at 5 cm/s. The extinguishment of hydrogen flames with Halon 1301 required 18.3 % v/v, in good agreement with the value of 17.7 % v/v reported by Creitz[21]. Hydrogen flames in the same apparatus were extinguished by 13.2% v/v FM-200®.

FM-200® was also found to be slightly superior to Halon 1301 on a volume basis for the inertion of hydrogen/air mixtures. Measurements performed at the University of New Mexico employing the NMERI explosion sphere indicated inerting concentrations of 24 and 25% v/v for FM-200® and Halon 1301, respectively[22]. The cup burner and explosion sphere results are shown in Table 5, which also compares the two agents on a volume and weight basis.

Summary

FM-200® has been shown to rapidly suppress the flaming combustion of Class A fuels at its minimum Class A design concentration of 7% by volume, and to rapidly extinguish Class B fires of various fire size to room volume ratios at the minimum design concentration for the particular fuel. For both Class A and Class B fires, the amount of HF produced following extinguishment with FM-200® is a linear function of the fire size to room volume ratio, for fire size to room volume ratios up to approximately 10. The extinguishment of Class A fires typical of those expected in an EDP facility with 7% by volume FM-200® produced HF concentrations of the same magnitude as the total decomposition products (HF plus HBr) produced upon extinguishment with Halon 1301, and for the extinguishment of Class B fires with FM-200®, the amount of HF produced is approximately 2 to 6 times the total decomposition product (HF plus HBr) produced upon extinguishment with Halon 1301. Rapid detection and discharge have been shown to allow for the control and reduction of thermal decomposition products following extinguishment of fires with FM-200®. The solubilities of air, argon, helium and carbon dioxide were measured experimentally. The solubilities of air, argon, helium and nitrogen in liquid FM-200® are all low and of the same magnitude, whereas the solubility of CO_2 in liquid FM-200® is higher by at least an order of magnitude.

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Finally, it was found that FM-200® is more efficient, on both a volume and mass basis, at the extinguishment of hydrogen flames compared to Halon 1301, and more efficient on a volume basis at the inertion of hydrogen/air mixtures compared to Halon 1301.

Figure 1. HF Concentration: Class A and Class B fires extinguished with 7%-8% FM-200®

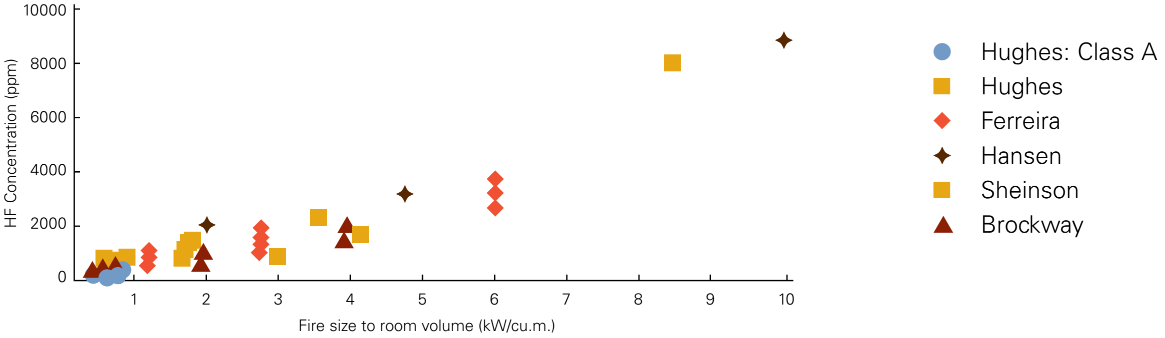

Table 1. Solubility Constant for Gases in FM-200® at 70˚F

Gas	**K x 10^4, psia^{-1}**
Nitrogen	2.03
Air	2.32
Helium	0.78
Argon	2.67
Carbon dioxide	17.0

Table 2. Amount of Nitrogen Required to Superpressurize FM-200® to the Indicated Total Pressure at 73.4˚ F; Fill Density = 58.2 lb/ft^3

P, psia	**lb N_2/lb FM-200® NIST**	**lb/N_2/lb FM-200® GLCC**	**% Deviation***
416	0.0226	0.0230	+1.8
432	0.0246	0.0241	-2.0
616	0.0370	0.0369	-0.3

* *100*(GLCC-NIST)/NIST*

Table 3. Suppression of Hydrogen Combustion

	EXTINCTION			**INERTION**		
	Ext. Conc., % v/v	**Efficiency**		**Inerting Conc., % v/v**	**Efficiency**	
		volume	**mass**		**volume**	**mass**
FM-200®	**13.3**	**0.7**	**0.8**	**24**	**1.0**	**1.1**
Halon 1301	**18.3**	**1.0**	**1.0**	**25**	**1.0**	**1.0**

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