THERMAL DECOMPOSITION PRODUCT TESTING WITH C_6 F-KETONE

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ABSTRACT

3M has developed a new class of compounds of which one, C_6 F-ketone (or perfluoro-2-methyl-3-pentanone, or $C_6F_{12}O$, or $CF_3CF_2C(O)CF(CF_3)_2$), has shown potential for both total-flooding and streaming applications [1]. This new fire protection fluid provides the right combination of performance, safety, and sustainable environmental properties as well as economic viability for commercial acceptance. Understanding the balance requires knowledge of the key properties and the extinguishing effectiveness. The thermal decomposition products (TDP) resulting when halocarbon alternatives are discharged to extinguish a fire has been studied. Work performed by 3M and others has shown that acid-gas production by halon alternatives is between **2** and 10 times greater than that of Halon 1301. It has also been shown that the three key factors resulting in thermal decomposition production are the fire size-to-volume ratio, the agent volumetric concentration, and the discharge time [2]. Testing conducted in 3M's 1.28 m^3 (45 ft^3) "box" included Class **A** fires and Class B fires. The three variables in the test matrix are fire size, agent discharge time, and agent concentration. TDP are then quantified using on-line FTIR analysis. The TDP data are compared with other commercially available halon alternatives previously tested. It should be noted that small-scale TDP testing for comparative purposes is only one method of determining the expected performance. Full-scale demonstrations incorporating actual field conditions can yield results not anticipated in small-scale tests.

INTRODUCTION

The halon alternative search for critical use applications, with the right combination of performance, safety, and environmental characteristics, has been the subject of considerable research by the fire protection industry over the past decade. While halons excel in performance and safety, the presence of chlorine and bromine in their molecular structure has been proven to be very destructive to the earth's ozone layer. It is therefore paramount for a replacement agent to be sustainable environmentally, not only with a zero ozone depletion potential (ODP) but with minimal persistence in the environment.

3M has developed a new class of compounds of which one, C_6 F-ketone, has shown potential applications as an alternative to commercially available halon replacements. C_6 F-ketone is perfluoro-2-methyl-3-pentanone, or $C_6F_{12}O$, or $CF_3CF_2C(O)CF(CF_3)_2$. The focus of this paper is an analysis **of** thermal decomposition products **(TDP)** testing and comparison to other commercial halon alternatives.

Studies such as those conducted by **M.** Meldrum and the Robens Institute provide analyses indicating levels at which TDP can be dangerous. Meldrum concluded that the dangerous toxic load (DTL), for various animals, *is* 12000 ppm-min, in other words, the DTL for a 30-min HF exposure is 400 ppm [3]. The Robens Institute study found that the highest tolerable HF concentration, for human subjects, was 120 ppm for a 1-min exposure [4]. Previous work done at 3M, and elsewhere, has shown that the main factors affecting TDP are duration of fire exposure, fire size, and agent concentration; therefore, a testing matrix was developed to consider fire size, discharge time, and agent concentration.

METHODOLOGY

TEST ENCLOSURE

Testing was conducted at **3M** in a 0.91 x 0.91 x 1.7 m^3 (3 x 3 x 5 ft^3) box, constructed of **1.3** cm *(0.5* in.) thick polycarbonate walls, reinforced with a 5 cm (2 in.) angle iron frame. This provides a 1.28 m^3 **(45** ft') total floodable volume. Two doors, located at different heights on opposing walls, allow access to the box once it is sealed. The doors are equipped with four compression latches and a rubber seal to ensure an airtight seal. The rest of the openings in the box are located on the other two walls. Ventilation is accomplished by an air inlet valve located near the bottom of the enclosure and another outlet valve located on the opposite wall and near the enclosure top. Both of these valves are controlled by solenoids. Three additional openings allow for 0.64 cm dia (1/4 in.) Swagelok™ bulkhead fittings, which can be used for gas sampling. Fires are located on the enclosure floor on a **7.5** cm (3 in.) riser. Surrounding the fire is a metal baffle, measuring **38** x **38** x 20.3 cm^3 (15 x 15 x 8 in^3), which is used to reduce turbulence around the fire and eliminate a possible blow-out of the fire. Figure 1 shows a complete schematic.

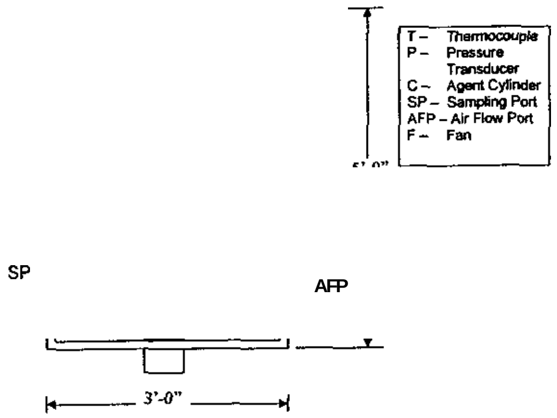

Figure 1a. Side view.

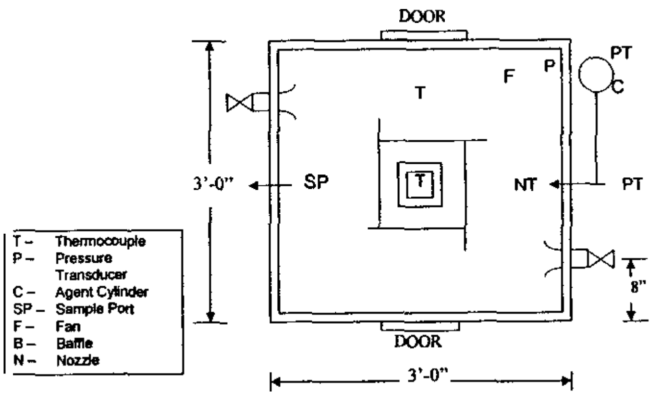

Figure 1b. Top view.

INSTRUMENTATION

The box is equipped with five Omega™ Type K stainless-steel thermocouples. A thermocouple tree, consisting of three thermocouples evenly spaced in the vertical direction, is oriented directly over the fire. The two other thermocouples are used to measure temperatures around the nozzle during discharge: one is located in the discharge stream 2.5 cm (1 in.) from the nozzle, and the other is located inside the piping immediately before the nozzle. Two Omega™ PX-102 sealed gauge pressure transducers with a working range of 0 to **344** kPa (**0** to 500 psi) measure pressure in the cylinder and at the nozzle. Data are collected by an Omega™ DaqBook 100 with one Omega™ DBK 19 card for pressure transducer data and one Omega™ DBK **13** card for thermocouple data. The data collection system is run by an IBM™ ThinkPad™ 600E using LabTech Notebook"" v 10.02 software.

DISCHARGE APPARATUS

Agent is stored in a **3.8 l (1** gal) Whitey™ stainless-steel cylinder fitted with a valve at the base. The cylinder is connected **to** the nozzle by a simple piping network of 0.64 cm dia (1/4 in.) pipe bolted to the exterior of the box, with a ball valve for discharge. The discharge nozzle is located on a side wall, centrally in the horizontal direction, on the upper quarter point in the vertical direction.

AGENT CONCENTRATION CALCULATIONS

Two agent concentrations were chosen: cup burner and cup burner + 20%. In accordance with NFPA 2001, the initial total volumetric agent concentration was determined as the cup-burner minimum extinguishing concentration for heptane, as established by a recognized testing lab. An increased agent concentration was based on the minimum heptane cup-bumer value plus a 20% safety factor. Agent mass required to produce the desired agent concentrations in the box was calculated as follows:

$$W = \frac{V}{s}\left(\frac{C}{100-C}\right)$$

where, W is the mass of the agent in lb (kg), V is the enclosure volume in ft^3 (m^3), C is the agent design concentration (vol %), and s is the agent specific volume at 1 atm. and ambient temperature [5].

DISCHARGE TIME

Discharge times of 3 s, 9 s, and 25+ s were chosen to compare with previous testing done [2, 6]. The discharge time is controlled by the flow rate (orifice size) of the discharge nozzle. Initial testing was conducted to determine the nozzles needed to produce the desired discharge time. The test results are presented in Table 1. The computer data acquisition allowed for the experimental determination of the discharge and extinguishing time for each test [7]. A typical pressure history **is** listed in Figure 2.

TABLE 1. NOZZLE DISCHARGE TIMES.

Aeent Concentration	Aeent Discharge Time		
	3 s	**9 s**	20+ s
Cup Burner **(4.9%)**	Spraying Systems, TP8020	Spraying Systems, TP8005	Spraying Systems, TP8001
Cup Burner + 20% (5.9%)	Spraying Systems, TP8020	Spraying Systems, TP8006	Bete Company, NF0300

FIRE SIZE

The four different fires sizes used in this study were chosen to compare with previous work [2, 6]. A cone calorimeter was used to determine the heat release rates of the four square pans, which measured 2 cm (0.75 in), 4.5 cm (1.75 in), 7 cm (2.75 in), and 9.5 cm (3.75 in). The corresponding heat release rates for these pans when filled with heptane are 0.1 kW, 0.6 kW, 1.7kW, and **3.7** kW, respectively. For each test, the pans were filled to the top with fresh heptane immediately before the test. New heptane is used for each test to prevent agent build-up in the fuel.

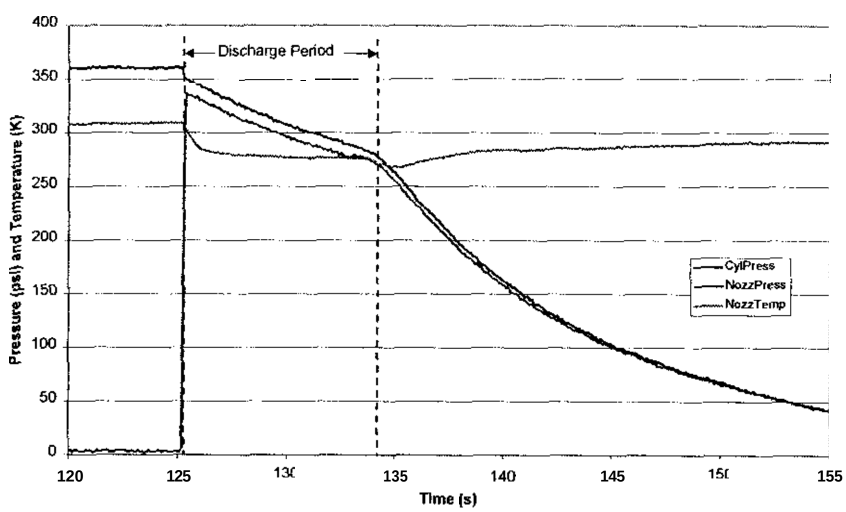

Figure 2. Typical pressure history for agent discharge into test enclosure.

FTIR ANALYSIS PROCEDURE AND SETUP

Two MIDAC I Series Model **FTIR** spectrometers were used for this field test. Each spectrometer was configured with a ZnSe beam splitter. A I-cm, unheated stainless-steel gas cell using ethylene as **a** diluent was used to acquire C_6 F-ketone concentration data. **TDP** concentrations, which are orders of magnitude less than C_6 F-ketone concentrations, were acquired using a 10-cm, unheated, stainless steel gas cell. The spectrometers had an ultimate resolution of 0.5 cm-1 unapodized and were coupled with 110V gas sampling pumps and portable computers for data acquisition.

The extractive gas sampling system used for the enclosure testing consisted of approximately 3 m of **0.64** cm dia PTFE tubing leading into the gas cells. Each spectrometer and its sampling system were operated independently. TDP samples were drawn from the box through a 3 m long, **0.64** cm dia PTFE sampling line into the spectrometers. Samples were continuously pumped through the sample line and the gas cells at a flow rate of 1 and 2 l pm for the 1-cm and 10 cm gas cells, respectively. Flows were verified on site using a Dry Cal™ flow meter. Three, 2.5 min spectra were taken for every test. The maximum HF concentration was determined by taking the greatest of the three spectra.

TEST PROCEDURE

Immediately before each test begins the calibrated heptane pan is filled to the top with heptane. The test begins when the fuel is ignited, at which time the access door is sealed and the FTIR machines are tumed on. The **60 s** prebum occurs with both the box inlet and outlet valves open, minimizing combustion product buildup and oxygen depletion. The valves are then closed, and 5 s later the agent is discharged. After extinguishment, the fan inside the enclosure is turned on to mix the enclosure volume thoroughly. The box remains sealed during the FTIR analysis cycle.

RESULTS

The maximum HF concentration is determined through FTIR analysis. Figure 3 presents results for Class B testing. The data are linearly regressed for comparison purposes. HF production is a monotonically increasing function of fire size. It is also seen that there is a relationship between the agent exposure time to the fire (i.e., discharge time) and the HF production.

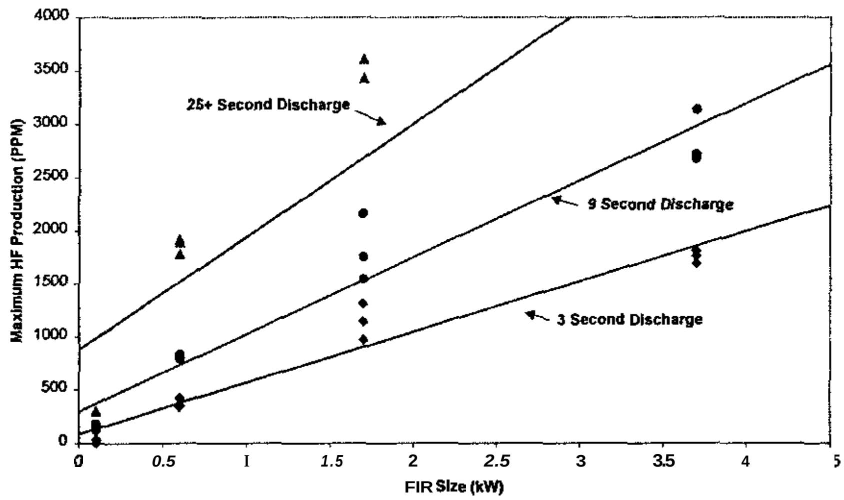

Figure 3. C_6 F-ketone maximum HF production vs. fire size (cup burner **4.9%** v/v).

C_6 F-ketone is also useful in extinguishing Class A fires. The HF production from the Class A fires is lower than for Class B fires (Figure **4).** This is consistent with previous work and shows that heptane was a good choice for a worst-case scenario for HF production [2]. Figure 5 compares the maximum HF production for various agents resulting from exposure to a fire. The fire sizes are normalized to allow the comparison of TDP irrespective of test compartment size. In terms of thermal decomposition production, C_6 F-ketone is directly comparable to other commercially available halon alternatives [3, 8].

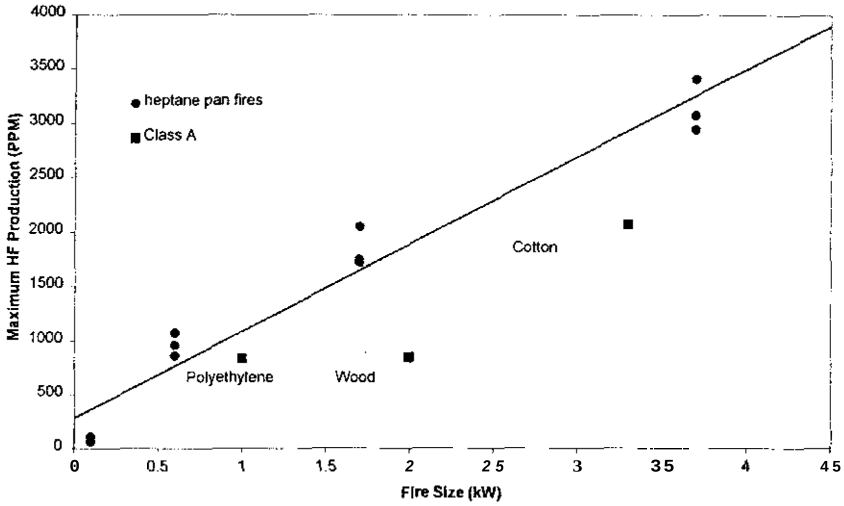

Figure 4. Maximum HF production vs. fire size (9 s discharge, cup burner + 20%).

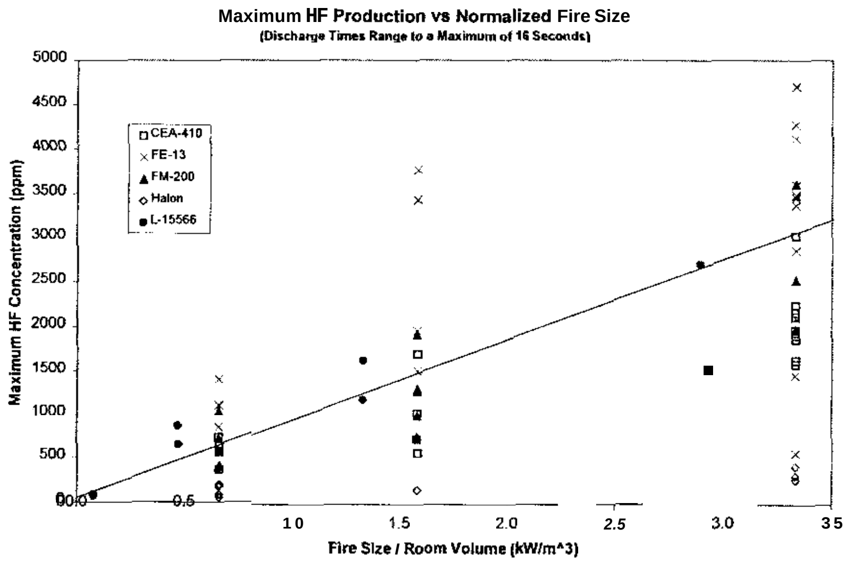

Figure 5. Comparison of TDP for halon alternatives (DiNenno et al *[8]* plus C_6 F-ketone data).

DISCUSSION AND **CONCLUSIONS**

The tests in this report are representative of fire conditions in real hazard scenarios. For example, the maximum fire size tested in this study is 3.7 kW, similar to the typical fire size for a circuit board, which is on the order of 3 to 5 kW according to industry experts. Figure 6 can be used as a tool such that the TDP can actually be predicted for a given room size. A system is then engineered to limit TDP below hazardous levels through effective design.

The importance of effective design is indicated by studies examining the effects of TDP exposure. One such study, conducted on animal subjects by M. Meldrum, sets the dangerous toxic load (DTL) at 12000 ppm min. In other words, the DTL for a 30-min HF exposure is 400 ppm [3]. The Robens Institute study conducted found that the highest tolerable HF concentration for a 1-min human exposure was 120 ppm [4]. Figure 6 shows that when typical room sizes are considered, in most cases, C_6 F-ketone produces tolerable levels of TDP.

C_6 F-ketone showed comparable performance in TDP testing to currently commercially available halon alternatives. The tests conducted showed the ability to extinguish fires with a variety of different fuels under a wide range of conditions. Note that small-scale TDP testing only provides a means for comparing performance; full-scale demonstrations should be conducted to validate small-scale results. Test results show a relationship between HF production and fire size as well as with discharge time and agent concentration. In all instances, a shorter exposure time to fire results in a lower TDP generation. The emphasis for system design should therefore be on early fire detection and rapid discharge.

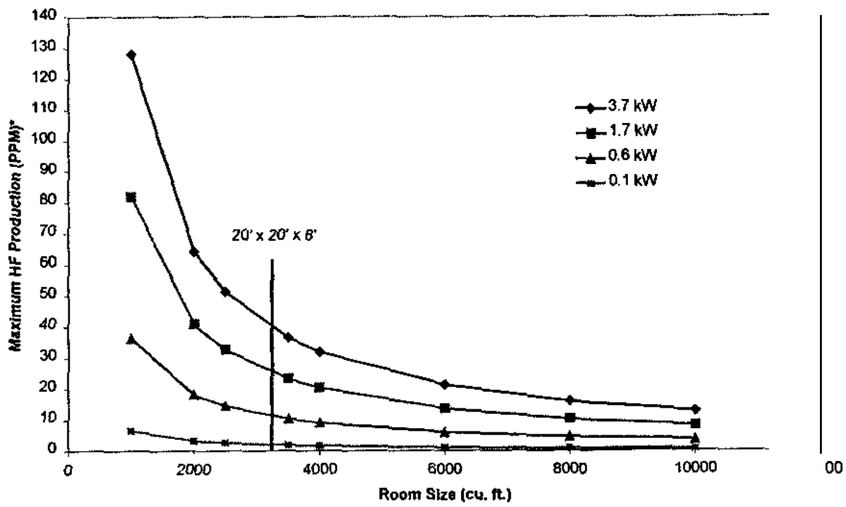

Figure 6. Calculated TDP concentrations for a “normal” sized room (C, F-ketone at 4.9%).

REFERENCES

1. Rivers, P.E., “Advancement in Sustainable Fire Protection Development C_6 F-ketone: A Novel New Halon Replacement Alternative to HFCs and PFCs,” ***Proceedings,*** Halon Options Technical Working Conference, Albuquerque, NM, this volume, 2001.
2. Ferreira, M.J., Hanauska, C.P., and Pike, M.T., “Thermal Decomposition Product Results Utilizing PFC-410 (3M Brand PFC-410 Clean Extinguishing Agent),” ***Proceedings,*** Halon Options Technical Working Conference, Albuquerque, NM, pp. 225-236, 1992.
3. Peatross, M.J., and Forssell, E.W., “A Comparison of Thermal Decomposition Product Testing of Halon 1301 Alternative Agents,” ***Proceedings,*** Halon Options Technical Working Conference, Albuquerque, NM, pp. 331-342, 1996.
4. Mann, A.H., “Possible Health Risks From Exposure to Hydrogen Fluoride Generated from the Use of Fluorinated-Containing Fire Extinguishing Agents,” prepared for 3 M by the Robens Institute, University of Surrey, Guildford, Surrey, United Kingdom, 1996.
5. NFPA 2001, ***Standardfor Clean Agent Fire Extinguishing System,*** 2000 Edition.
6. Brockway, J, “Recent Findings on Thermal Decomposition Products of Clean Extinguishing Agents,” NFPA 2001 Technical Committee on Alternative Protection Options to Halon, Meeting Minutes, p. H-5, Ft. Lauderdale, FL, 1994.
7. DiNenno, Phillip J. et al. eds., “Halon Replacement Clean Agent Total Flooding Systems,” ***The SFPE Handbook of Fire Protection Engineering,*** 2nd Edition, Section 4, Chap. 7, 1995.
8. DiNenno, P.J., Forssell, E.W., Peatross, M.J., and Maynard, M., “Thermal Decomposition Product Testing of Halon Alternatives” ***Proceedings,*** Halon Options Technical Working Conference, Albuquerque, NM, pp. 161-184, 1993.