THERMAL DECOMPOSITION PRODUCT RESULTS UTILIZING PFC-410 (3M BRAND PFC-410 CLEAN EXTINGUISHING AGENT)

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INTRODUCTION

Halons have long been the agents of choice in protecting fire hazards which necessitate the use of a clean, safe, and effective extinguishing agent. These agents, however, have been shown to have a destructive effect on the earth's ozone layer, due to the presence of bromine and chlorine in their molecular structure. As a result, under the provisions of the Montreal Protocol, halon production will be phased out by the year 2000, creating the need for replacement clean agents which can function in critical applications currently utilizing halons.

3M has investigated the perfluorocarbon family of compounds for possible applications as halon replacements. As a result, perfluorobutane (C_4F_{10}) has been identified as a total flooding replacement for Halon 1301 in certain applications. Perfluorobutane (the CFC designation currently being used by the National Fire Protection Association is FC-3110) will be referred to in this paper by its 3M product code, PFC-410.

PFC-410 is currently undergoing extensive testing at 3M. Initial cup burner results proved that the agent would extinguish a wide variety of fuels with reasonable extinguishing concentrations. Tests to validate the cup burner data were conducted in a 500 cubic foot room, extinguishing heptane, methanol, and wood crib fires. These tests showed the effectiveness of PFC-410 in fire scenarios.[1]

In order to collect more data on extinguishment phenomena, agent performance, and thermal decomposition product formation, 3M contracted Hughes Associates, Inc., to construct a fully instrumented fire test apparatus. To date this apparatus has been used to conduct over 100 tests using PFC-410, yielding preliminary extinguishment and thermal decomposition results.

THE AGENT

PFC-410 is a clean fire extinguishing agent, it will completely vaporize and require no clean-up after a system discharge. It is a very stable, inert, and electrically non-conductive gas. Thus, it can be safely used to protect electronic equipment Physical property data for **PFC-410** can be found in Table **1,** while cup burner data can be found in Table 2.

Because **PFC-410** does not contain chlorine or bromine, the atoms responsible for ozone depletion, its ozone depletion potential **(ODP)** is zero. It will not conmbute to breakdown of stratospheric ozone. The stability of **PFC-410** gives it a relatively long atmospheric lifetime, but preliminary analysis indicates that the potential contribution to global warming is negligible.

A mcdel which allows for the prediction of the contribution of perfluorocarbons to global warming has been developed by Atmospheric and Environmental Research, Inc. of Cambridge, MA. For **PFC-410,** this model assumes increasing production to a peak of **5** million pounds per year after 10 years, sustained production at that level for **10** years, and finally decreased production down to zero over the final **10** years. It also assumes that all **PFC-410** produced would be released into the environment. **For** production at these levels, the model predicts a **0.00017 °C** global temperature rise over 100 years.[2] This number is orders of magnitude less than the **4-5 °C** temperature rise expected from CO_2 and methane alone. Also, it has been suggested by leading researchers in atmospheric science that compounds contributing less than 0.005 **°C** over **50** years will have a negligible impact on global warming.[3]

It should be noted that two of the parameters in obtaining the model's low global warming estimate are already over-exaggerated. In reality, 3M expects production levels for **PFC-410** to be less than those used in the model. Most of the agent produced will also be kept in enclosed systems, and not released into the environment as the model suggests. It will be recycled whenever possible. Therefore, the potential global warming effect will be reduced even further from what the model shows is already negligible.

TEST APPARATUS

3M's alternative agent test enclosure is a 3 x 3 x 5 foot (*.91* x **.91 x 1.7 m**) "box" constructed from 0.5 inch **(1.3** cm) thick polycarbonate sheet and reinforced by a frame constructed from 2 inch *(5* cm) angle iron. It provides a **45** ft3 **(1.3** m3) floodable volume. Two portals are provided on either side of the enclosure at different heights for full access to its interior.

Compression latches allow for these doors to be sealed tightly during test runs. The enclosure also has an inlet valve near the bottom and an outlet valve near the top, both of which can be sealed using solenoid valves. Three more sealable openings, for gas sample bottles, penetrate one of the walls. The enclosure is shown in Figures 1 and 2.

Discharge of agent into the test enclosure is achieved through a simple 0.25 inch (.64 cm) pipe network bolted to the side of the test enclosure and connected to a fixture in the side of the enclosure to which various size nozzles can be attached. A removable discharge cylinder is connected to the pipe at the side of the test enclosure, with a quarter turn valve at one end for cylinder filling and a valve at the other to control agent discharge. The discharge system is shown in Figure 3.

The test enclosure is instrumented with a load cell, located in the center of the floor of the box. The fuel pan sits on this load cell during the tests. One thermocouple tree, consisting of five thermocouples evenly spaced in the vertical direction, lies over the centerline of the fire. Another identical thermocouple tree is placed 4 inches (10 cm) from a wall. Pressure transducers record enclosure pressure, as well as cylinder and nozzle pressure. An oxygen analyzer, with a sampling tube that penetrates the floor of the enclosure, records oxygen concentration within the enclosure during the test runs.

With the exception of gas sampling bottles, all data is collected electronically and stored in a data file. Data collection is enabled by a Metrabyte DAS-8 analog to digital conversion board with two Metrabyte EXP-16 multiplexor cards, driven by the PC based Labtech Notebook software package.

TEST PROCEDURE

Once the fire is ignited in the fuel pan, using a model rocket ignitor, a 60 second pre-burn time is allowed to ensure the fire has reached steady burning. The pre-burn occurs with both inlet and outlet valves open in order to minimize combustion product buildup and oxygen depletion. The valves are then closed and the agent discharged. The fuel pan has been shielded by a movable 6 inch (15.25 cm) high, 15x15 inch (15.25x15.25 cm) baffle. It was shown in early tests in the enclosure that without the baffle, blow-off caused by agent turbulence seemed to be a significant factor in the extinguishment of the fire, especially at smaller fire sizes.

Table 1. Chemical and Physical Properties

Chemical Formula	Halon 1301 $CBrF_3$	PFC-410 C_4F_{10}
Molecular Weight	148.9	238
Heat of Vaporization KJ/g mol (BTU/lbm. mol)	12.3 at 21 °C (5292 at 70 °F)	22.8 at -2 °C (9801 at 28°)
Normal Boiling Point	-57.8 °C (-72 °F)	-2.2 °C (28 °F)
Vapor Pressure MPa (psia)	1.47 at 21 °C (213,7 at 70 °F)	0.330 at 32 °C (47.9 at 90 °F)
Critical Temperature	67 °C (152.6 °F)	113.2 °C (235.8 °F)
Critical Pressure	3.97 MPa (575 psia)	2.32 MPa (337 psia)
Vapor Density kg/m^3 (lmb./ft^3)	6.26 at 21 °C and 0.101 MPa (0.391 at 70 °F and 14.7 psia)	9.94 at 25 °C and 0.101 MPa (0.620 at 77 °F and 14.7 psia)
Liquid Density kg/m^3 (lbm./ft^3)	1567 at 21 °C (97.8 at 70 °F)	1517 at 20 °C (94.6 at 68 °F)

Table 2. Cup Burner Extinguishing Concentrations - PFC-410 (At 25 °C)

	Concentration %	
FUEL	PFC-410	HALON 1301
Heptane	5.9	3.7
Acetone	5.5	3.6
Ethanol	6.8	4.7
Methanol	9.4	7.8

Note: This data was obtained by using the standard "Cup Burner" test method. This method is considered to give reliable extinguishing concentration data. However, the concentrations can vary somewhat with the particular apparatus. The data is most useful when compared to a standard such as Halon 1301 collected from the same apparatus.

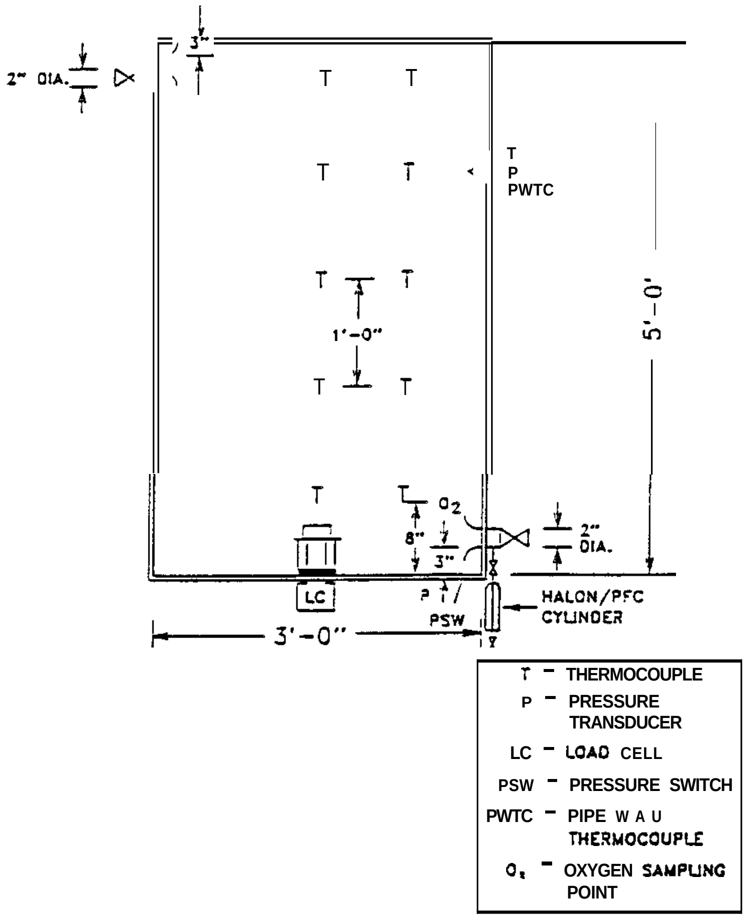

Fig. 1 - Elevation view

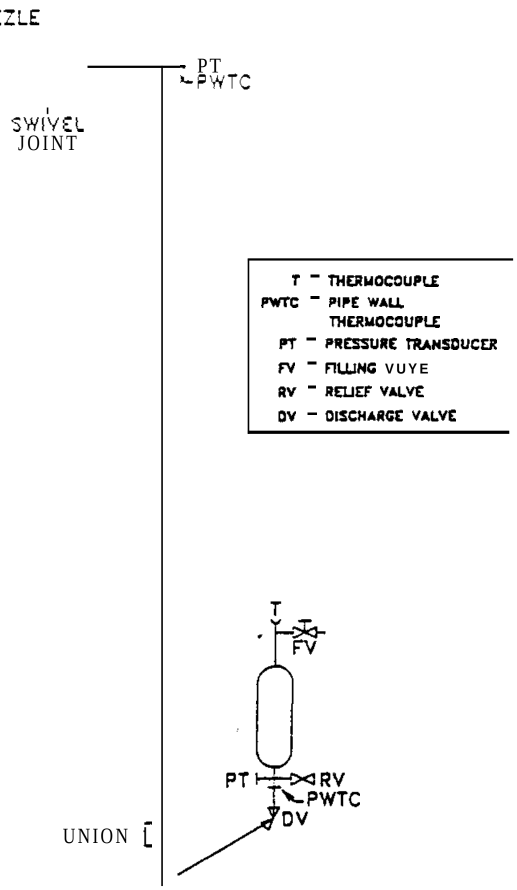

Fig. 3 - Discharge system

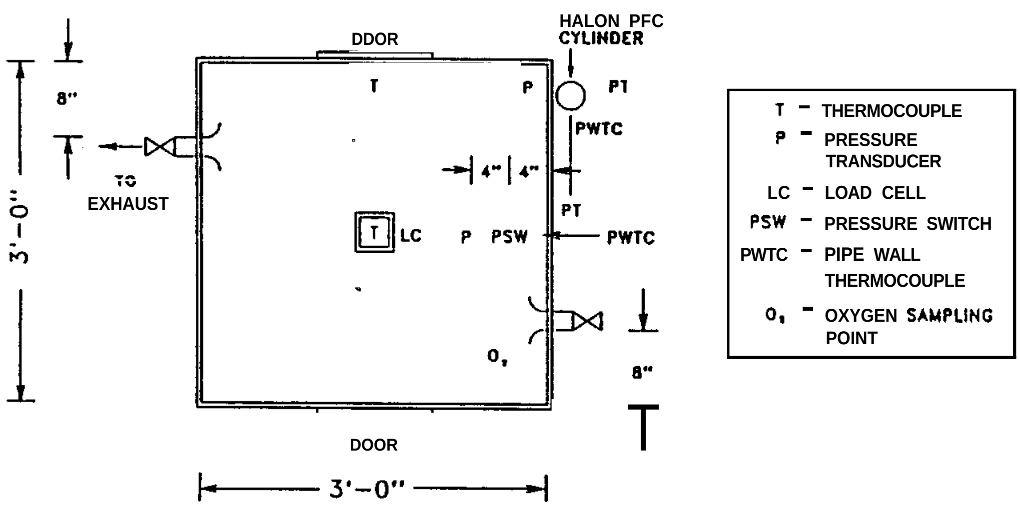

Fig. 2 - Plan view

Immediately after tripping the switch indicating extinguishment, the test operator turns on a 4 inch (10 cm) diameter fan mounted in a lower comer of the test enclosure. This fan is allowed to run for 30 seconds, at which time a sample is taken in an evacuated bottle, for thermal decomposition product (TDP) analysis. The fan is used to *mix* the TDP's to a uniform concentration within the enclosure. Preliminary results showed a stratification of TDP concentration when samples were taken at three evenly spaced heights, without the fan. Further testing confirmed that very little TDP deposited onto the interior surfaces of the test enclosure during the 30 seconds the fan was running. Therefore, the one sample taken after 30 sec. fan time was representative of an average TDP concentration for the interior volume of the test enclosure.

THERMAL DECOMPOSITION PRODUCT TESTING

Samples for thermal decomposition analysis were collected in evacuated plastic gas sampling tubes which had been precoated with a thin layer of sodium hydroxide. Water was added and the solutions were analyzed for F^- using a fluoride ion specific electrode. Since previous 3M and outside testing had shown decomposition products for PFC-410, and perfluorocarbons, in general, to be mainly acid fluoride gases and lower molecular weight perfluorocarbons[4], this study was resmcted to quantification of the fluoride acid gases. These react with sodium hydroxide to yield fluoride ion. While COF_2 and perfluoroacyl fluorides were found in small amounts, the predominant TDP was HF. No other toxins were identified in any of these tests. In the tables and figures that follow, the *amount* of TDP formed is reported in ppm, assuming that all of the fluoride detected came from HF.

Minimum extinguishing concentration tests in sets of five were run at various agent concentrations, using heptane fuel and an 8-8.5 second discharge time, to create a profile of extinguishment time vs. Concentration (Figure 4). This graph shows good repeatability *of* results with greater than 5% agent concentration. Below 5% agent concentration results varied significantly, as agent concentration became too low to directly extinguish the fire and reduced oxygen concentration within the test enclosure became a factor. Extinguishment in this range of agent concentration will be the focus of further study.

Cup burner extinguishment tests for PFC-410 have been carried out at 3M and other test facilities and have shown minimum extinguishing concentrations for heptane fuel ranging from 5.1% to 5.9%. Taking the average of this range (5.5%), and an approximate 20% safety factor, a ***6.5%*** "design" concentration was arrived at for the TDP tests. Results had been shown to be consistent at this agent concentration, and all of the heptane **fires** had been easily extinguished.

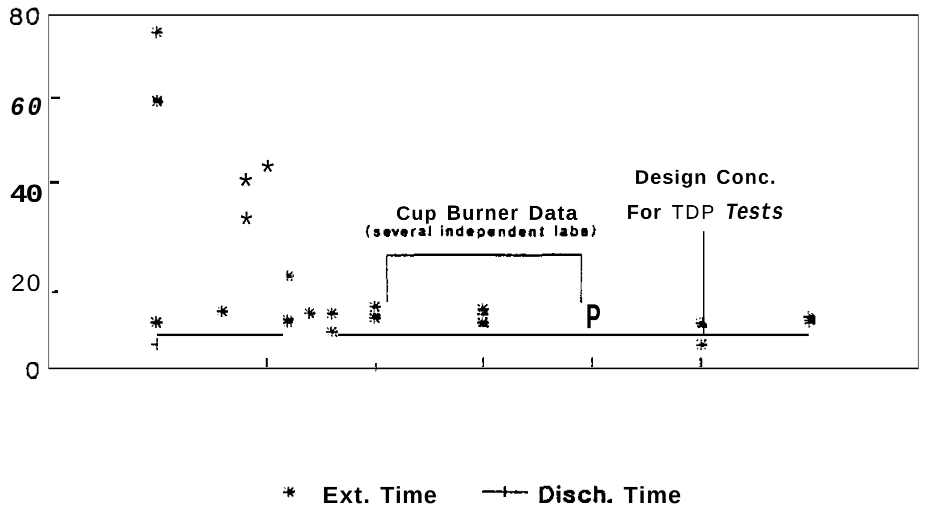

Figure 4. Minimum Extinguishing Concentration Tests

Once ***6.5%*** had been chosen for the design concentration for this study, the following sets of tests were carried out:

1. Constant fire size **(3.2**kW), varied discharge time.
2. Constant discharge time (8-8.5 seconds), varied fire size.
3. Limited Class **A** Testing.

The first two sets of tests were designed to establish initial relationships between parameters affecting the amount of acid gas created in extinguishing various fiis. The Class **A** tests were designed to show PFC-410's ability to put out fires, as well as to provide a limited comparison to heptane fire results.

RESULTS

For all of the tests, oxygen concentration levels did not fall below about 18%, meaning that the fires were extinguished long before oxygen depletion became a problem. Data for the Class **A** tests can be found on Table 3, while data on the discharge time and fire size tests can be found on Table 4 and Table 5.

Table 3. Class A Fires
(NF2000 Nozzle)

TEST#	FUEL	AMT, g	DISCH. TIME (Sec)	EXT. TIME (Sec)	FIRE SIZE (kW)	TDP (PPM)
1	Wood	10	7.8	7.1	4.44	545
2	Cotton	40	8.2	7.1	6.92	1107
3	Polyethylene	25	8.0	4.3	2.46	358

As was expected, there is a direct correlation between agent discharge time and amount of acid gas created, as shown in Figure 5. The longer the fire was exposed to agent before the enclosure reached extinguishing concentration, the more acid gas was produced. While this relationship seemed to be linear, more data will need to be collected. It should be noted that if a line were drawn through the data points on Figure 5, the y-intercept would be about 400 ppm of acid gas. This means that theoretically, if the discharge time were zero, acid gas would still be produced. Regardless of the discharge time, the fire needs to be exposed to agent in order to be extinguished, yielding thermal decomposition products. It should also be noted that in the range of 5 to 15 second discharge time, the difference in acid gas produced is relatively small.

Figure 5: TDP vs. Discharge Time
(3.2kW Fire, 45 ft^3 Enclosure)

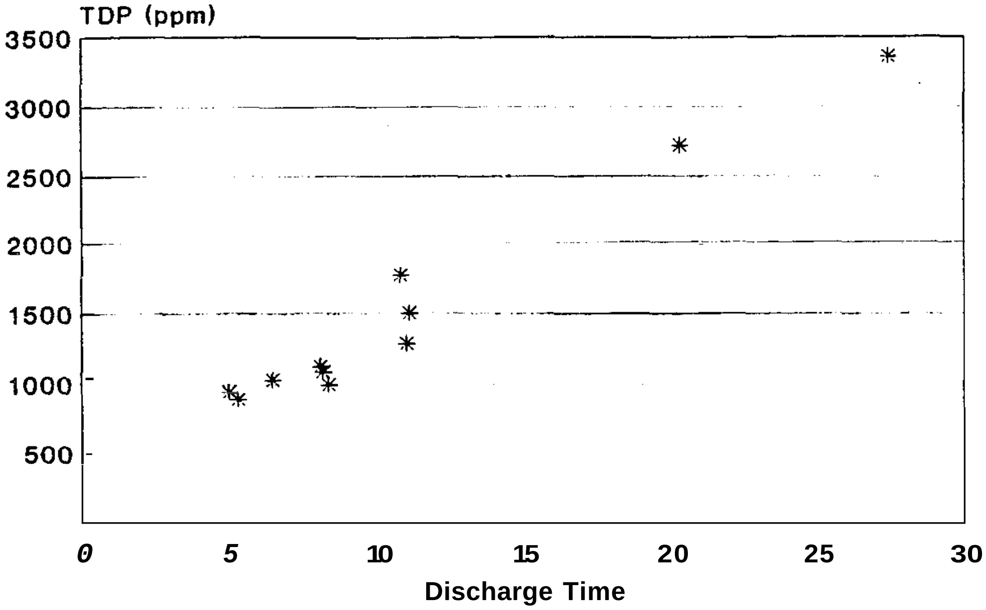

Figure 6: TDP **vs.** Theoretical Fire Size
***(8-8.5sec. Discharge** Time)*

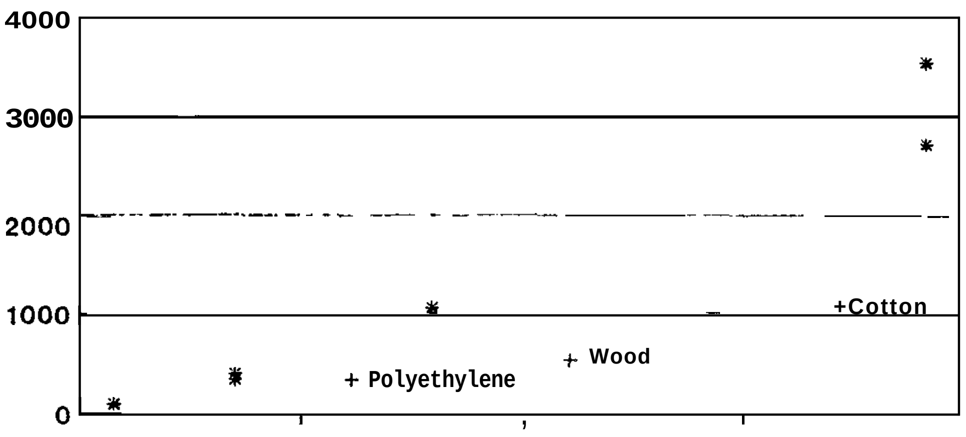

Table 4. Varied Discharge Time
(3.2kW Fire, Heptane Fuel)

TEST #	NOZZLE	DISCH. TIME (Sec)	EXT. TIME (Sec)	TDP (PPM)
1	NF500	27.4	24.4	3358
2	NF1000	20.3	20.8	2724
3	NF1500	11.0	8.8	1289
4	NF1500	11.1	11.8	1507
5	NF1500	10.8	11.0	1780
6	NF2000	8.4	10.1	999
7	NF2000	8.1	8.2	1128
8	NF2000	8.2	8.0	1089
9	NF3000	6.5	7.3	1035
10	NF4000	5.0	7.5	944
11	NF4000	5.3	5.8	890

Table 5. Varied Fire Size
(NF2000 Nozzle, Heptane Fuel)

TEST#	PAN SIZE (Square Pan)	FIRE SIZE (kW)	DISCH. TIME (Sec)	EXT. TIME (Sec)	TDP (PPM)	FLAME AREA TO 1000 ft^3 ENCLOSURE VOL. RATIO
1	10.75	0.3	8.2	6.7	98	0.576
2	0.75	0.3	8.3	7.2	90	0.576
3	1.75	1.4	8.1	11.6	275	6.40
4	1.75	1.4	8.2	7.6	336	6.40
5	2.75	3.2	8.2	8.4	999	16.2
6	2.75	3.2	8.2	8.5	1071	16.2
7	3.75	7.7	8.2	7.9	3540	31.9
8	3.75	7.7	8.4	6.5	2723	31.9

Results of tests with constant agent discharge time, for four different fire sizes, are shown on Figure 6. The amount of acid gas produced is plotted against theoretical heat release rate, determined for the different size heptane pan fires. The data seems to indicate a parabolic relationship. The relationship between acid gas formation and either fire size or theoretical flame surface area will be developed as more data is collected. From the graph, it can be seen that creation of acid gas is more dependent on fire size than on discharge time. If the fire was very small, approaching 0 kW, when extinguished, no acid gas would form. For bigger fire sizes, the amount of acid gas produced seems to increase exponentially. This, as expected, places importance on extinguishing the fire while it is relatively small.

Tests using PFC-410 to extinguish Class A fires showed that the agent has the ability to extinguish a variety of burning fuels. TDP results seemed to be within the expected ranges. When acid gas formation for Class A fires was plotted along with heptane fire data on Figure 6, less acid gas formation was shown. Therefore, heptane was shown to be a good fuel to use for our testing, a "worst case" for acid gas formation. More complete testing using Class A fuels will be conducted in the future.

CONCLUSIONS

PFC-410 showed good performance in extinguishing heptane and Class A fires. 3M's test enclosure has been shown to produce reliable extinguishment and decomposition data over a wide range of conditions, and will continue to be used to evaluate the performance of PFC-410 under these changing conditions. While full scale testing may be necessary to confirm the data collected in these smaller scale tests, results obtained utilizing 3M's test enclosure will serve as an effective method of comparison, as well as provide background data for design of the larger scale experiments.

Test results showed that definite relationships exist between acid gas TDP formation and agent discharge time and fire size. While shorter system discharge times are possible, little comparative difference in TDP exists over the range currently designed for. Emphasis on detection and extinguishment of fires at smaller fire sizes seems to have a greater effect on limiting the amount of harmful thermal decomposition product produced. More work will be done to quantify these relationships.

PFC-410 holds considerable promise as a clean, safe, total flood fire extinguishing agent. 3M will continue development efforts with the goal of having listed and approved systems commercially available in 1993.

REFERENCES

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