REDUCED HI: PRODUCTION WITH THE USE OF ADDITIVES

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INTRODUCTION

The reason for all of the activity over the last *so* many years and the reason for this, the ninth HOTWC conference, is to discuss halon replacements subsequent to the Montreal Protocol and to solve the problems that have arisen in that pursuit. Detoxification of fire extinguishment products goes back to studies done by NASA in 1986 by the Lyndon B. Johnson Space Center and White Sands test facility [1], ***NASA Tech Briefs***, March/April 1986 where ammonium compounds were inserted into fires with halon to successfully reduce HF production of the "wonder gas" halogenated agent. In subsequent fire testing done on a gelled powder/gas enhanced halon replacement in the NMERl field-scale test chamber during May-June 1995, little or no decomposition products (HF. CO, or COF_2) were measured (Perkin - Elmer FTIR) [2]. This created an interest and need for continued research into additive effects on **HF** generation, particularly directed to gaseous halon replacements that have demonstrated a greater affinity for HF production in fire scenarios.

Test Reasoning, Fixture, and Scenario

In the theory of what appeared reasonably evident, a program for further investigation of additives with prescribed gaseous halon replacements was pursued. Toward that end. two series of tests were conducted at the Aberdeen Test Center (ATC) in conjunction with Army Research Laboratories (ARL) to diagnose the mechanics of HF generation and better understand the **HF** reductions previously observed [3,4]. The tests were similar in configuration, using a 2.5 lb Metalcraft CO_2 handheld fire extinguisher (104 in^3). The extinguishers were inverted with the dip tube removed and connected through tubing to a modified nozzle in the top center of the test fixture box. The nozzle had 4 holes (0.041 dia.) oriented radially YO degapart and firing horizontally cross the top of the chamber. Tests were conducted against a 3.625 in diameter heptane pan fire inside a 1.5 m' enclosure. The fire pan was placed on a bottom shelf of a 16 in square table, ***3*** in above the floor in the center of the enclosure, with the upper shelf approximately 24 in above the fire pan serving as a baffle to afford a hidden fire total-flood scenario and avoid the possibility of any agent impingement on the fire. A 4 in circulating fan was installed near ceiling level and remotely activated to homogenize the gas mixture inside the chamber after the fire was extinguished and to reduec the stratification of compounds. During each trial the fuel was ignited, the chamber closed and fuel allowed to burn for 15 sec before the agent was discharged.

HF concentrations were measured using several techniques. Ignoring original tests using FTIR in ATC report LFV-46-97 (which was done outdoors) and creating ambient and humidity variations. the succeeding indoor tests used:

- Gas phase HF concentrations were measured using a near-infrared (NIR) tunable diode laser (TDL) mounted atop the fire stand inside the test chamber.
- Gas and liquid phase fluoride concentrations were measured using two analytical techniques developed and operated by the US Army Center for Health Promotion and Preventive Medicine (CHPPM). The first technique was a silica sorbent tube recommended by NIOSH in Method 7903 for measuring inorganic acids in air. The second method was a liquid and gas-phase fluoride ion-selective electrode analyzer developed by CHPPM.

Post-test solid phase residue samples of reacted and unreacted APP powder additive were collected in scattered petri dishes and analyzed by the ATC Chemistry Branch using an FTIR microscope technique to characterize the fluoride in the solid material. The test conditions and hardware were selected to create reproducible HF concentrations in the range of 1000-2000 ppm, not to optimize the performance of the extinguisher or extinguishant. For each mixture, the extinguisher pressures were adjusted to produce approximately 10 sec discharge times. Discharge times were verified by video and in off-line tests.

In these tests, the gaseous agent concentrations were selected to be approximately 7–7.5% concentrations (771 gms FE-36, 804 gms FM200), and it was decided to keep the HF generators at a constant level rather than to reduce gas levels to afford similar total agent charge. The study was to research HF production and, even though fire-out time is a proven factor in HF generation or reduction, we had to start somewhere. As the data will show, similar fire-out times did demonstrate HF reduction with the use of additives (Table 1). These tests of FE36 and APP additive at 15 wt.% indicate the HF concentrations possible. Every day of testing (5–7 tests/day) included an opening and closing test of pure gaseous agent to provide consistency of instrumentation and data generation.

TABLE 1. COMPARISON OF HF CONCENTRATIONS WITH EQUIVALENT FIRE-OUT TIMES [3].

Neat FE-36		FE-36 + 15% EG	
HF Conc. (ppm)	Fire-Out (sec)	HF Conc. (ppm)	Fire-Out (sec)
1502	9.22	201	9.6
1113	7.45	261	7.55

Mechanical difficulties did occur with extinguishers that were not designed for so many multiple tests even though they were torn down and rebuilt after each test. Leakage began to occur in the middle tests before firing and caused erratic data. New extinguishers were used for the 12 and 17% testing and demonstrated a possibly better distribution of agent and thus better characteristics (fire-out times) than other additive concentrations.

During the latest set of tests SL-36-98 [4] several tests were conducted in which the additives were introduced into the test fixture after the fire was extinguished by the pure gaseous agent (FM200), but at the point of maximum HF production, 1–2 sec after extinguishment. The additives were APP (ammonium polyphosphate) and $NaHCO_3$ (bicarbonate of soda).

The purpose of these particular tests was to eliminate the influence of the improved fire suppression capabilities of the enhanced gaseous agent to see whether either powder additive reduced HF concentration through chemical scavenging or deteriorated the HF concentration faster than if no powder was present at all. These tests indicated that the presence of powder reduces the HF from the enclosure, but, apparently, not through any chemical scavenging or reaction. Conjecture would say that the increased surface area of the powder particles helps to improve the rate of deterioration of the HF or decrease the rate of generation of HF. A question arose relative to the different particle sizes of the additive agents, which might be related to the HF reduction characteristics of the additive rather than their reaction or scavenging capabilities.

At the conclusion of each trial, the test and data collection equipment was removed and the interior of the test chamber was sprayed with a saturated solution of sodium bicarbonate and then thoroughly rinsed with water to neutralize and remove any residual HF. This cleansing was quality checked by HF measurements prior to each subsequent test.

All of these tests were conducted primarily using varying percentages of the powder additive ammonium polyphosphate in two gases, FE-36 and FM-200.

SUMMARY OF RESULTS AND CONCLUSIONS

The analysis of the TDL measurements of the gaseous portion of the HF generated indicates that the time rate of change of deterioration of HF of fires extinguished by FM-200 alone is not significantly different from FM-200 containing APP. As mentioned earlier, the solid phase analysis did not indicate any significant chemical reaction between APP and HF.

But. fires extinguished with only FM-200 or FE-36 produced unacceptably high HF levels. while all the varying degrees of the additive present, reduced HF to a lower level than the gases alone. The powder additives reached a level of HF generated, which appears acceptable to reported EPA standards of (100 ppm over 10 min) at 20 and 15% powder, respectively, when gelled with FM-200 and FE-36.

Based on the slope characteristics of the HF generated, chemical scavenging does not appear to be the dominant characteristic, but, at the same time, the HF generation figures do not lie (Table 2). The search continues to understand the possible additive behaviors that are causing these results.

TABLE 2. AVERAGE MAXIMUM TDL AND SORBENT TUBE MEASURED HF CONCENTRATIONS (PPM).

		% APP				
	FM-200	*20*	17	15	12	10
TDL	2667	120.1	722.8	1638.1	641.8	1858.4
Sorbent tube	3562	Below **detectable levels**	1511	***2732***	1254	3192

You will note the sorbent tube measurements are approximately double the TDL gas-only measurement since the sorbent tube is measuring all fluoride produced.

The presence of the tested APP shows a drastic reduction in the generation of HF and all the toxic and corrosive characteristics involved. Something in the presence of the APP and possibly other additives disrupts the ability of all HFC halon replacements to generate hydrogen fluoride. The reduction is clearly evident. How the reduction occurs is, for the moment, irrelevant to the fact that the reduction has been accomplished. Thermocouple measurements close to the fire did not show drastic temperature reductions, but any further testing should better define this as a possible contributor to the mechanics of HF reduction. Theory would dictate that some fluoride reaction is taking place in the HF generating fire zone, but that is not the subject of this paper. This report is just to demonstrate the test results.

In addition to the reduction of HF, not just toxicity is reduced to acceptable levels but corrosion is also reduced. Anyone who has witnessed multiple tests has seen how rapidly the hardware is attacked.

In selecting a HF reducing additive, its corrosive characteristics should be strongly considered, which was one of the main reasons so much emphasis in these tests was directed toward the use of APP, its multiple hazard (A,B,C) capability and its minimally corrosive nature.

There are a myriad of tests for corrosion, but the one chosen for APP was ASTM 1110-90, the Standard Test Method for Sandwich Corrosion [5], which is applicable to aircraft structural aluminum alloys. The interpretation of the results rank and rate the selected agent as being less than, equal to, or more corrosive than the Deionized (Reagent) water that acts as the control. The tested panels are given a numerical rating from 0 to 4, where 0 is no visible corrosion and 4 is excessive corrosion or pitting. Any corrosion in excess of ***3*** is cause for rejection.

Results

The corrosion ratings of all test panels used in this test at the Corrosion Testing Laboratories (Newark, DE) are given in Table 3. Based upon our interpretation of the results, the APP test material is considered to be acceptable from a sandwich corrosion standpoint.

TABLE 3. CORROSION RATINGS.

Condition	Alloy 2024 Anodized	Alloy 2024 Alclad	Alloy 7075 Anodized	Alloy 7075 Alclad
APP+DI water	3/3	1/1	3/3	1/1
APP dry	1/1	1/1	1/1	1/1
APP+gel	2/2	1/1	1/1	1/1
DI water	3/3	414	3/3	414

These, in essence, are the results of many tests concerning hybrid agents to establish toxic byproduct reduction, corrosivity acceptability, and improved fire-kill, which have been conducted in the search for a “drop-in” halon replacement.

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