This is a repository copy of *Fluorinated halon replacement agents in explosion inerting*.

Fluorinated Halon Replacement Agents in Explosion Inerting

Josephine G. Gatsonides[a,b], Gordon E. Andrews[b] ,Herodotos N. Phylaktou[b] & Adam Chattaway[a]
E-mail: josephine.gatsonides@utas.utc.com
a UTC Aerospace Systems, Colnbrook, UK
b University of Leeds, Leeds, UK

Abstract

The US Federal Aviation Administration (FAA) observed during explosion tests that at low concentrations candidate halon replacement agents increased the explosion severity instead of mitigating the event. At UTC Aerospace Systems a test program was developed to assess the behaviour of alternative agents at values below inerting concentration. Two agents were selected, HFC-125 and Novec™1230. Baseline tests were performed with unsuppressed propane/air mixtures and fuel/air mixtures with Halon 1301 and nitrogen (N_2). Using Halon 1301 or N_2 at below inerting concentrations mitigated the explosion. HFC-125 was tested against propane at stoichiometric (4 vol%) and lower explosion limit (LEL) (2 vol%). Against 4 vol% propane the combustion was mitigated, proportional to agent concentration; however, low concentrations of HFC-125 with 2 vol% propane enhanced the explosion. Tests with N_2 against a volatile mixture of propane with HFC-125 showed that N_2 mitigated the events. Final tests were performed with low concentrations of Novec™1230 against propane/air mixtures. This showed similar behaviour to that observed with the HFC-125 tests. Normally during qualification tests for new agents the stoichiometric concentration of a fuel is deemed to be the worst case scenario and the baseline against which agents are tested. The above described test results show that this assumption may need to be reconsidered. This work shows that contrary to common assumption the agents investigated did not act chemically at the flame front, but mainly cooled the flame and changed the stoichiometry, i.e. the ratio of components of the flammable mixture.

Keywords: gaseous suppressants, clean agents, inerting, mitigation, gas vapour explosions

1. Introduction

A number of halon replacement agents have been developed as acceptable alternatives for industrial fire protection applications. Some of these alternatives have been subjected to tests to assess their suitability for use in aerospace applications. During qualification tests at the US Federal Aviation Administration (FAA) test facilities unexpected agent behaviour occurred (Reinhardt, 2004). It was observed during explosion testing that at low concentrations certain candidate agents increased the explosion severity instead of mitigating the event.

1.1 Previous research into flammability of halon replacement agents

The US National Institute for Standards & Technology (NIST) carried out significant amounts of fundamental work on various halon replacements. Several of their publications refer to observed unusual behaviour. Grosshandler (1994) compared halon alternatives and measured unusually high pressure ratios for a mixture containing CH_2F_2 and C_2HF_5 (HFC-125) and significant pressure increases at lean ethane/air mixtures. Further investigation into suppression of high speed flames led to his conclusion that the tested agents could either enhance or suppress combustion, depending on their volumetric concentration. HFC-125 at

concentrations of 5 vol% showed the highest increase in severity of deflagration (Grosshandler, 1997).

Theoretical research into the possible causes for these phenomena included development of calculation models to describe and predict the mechanisms of the specific explosion events (Linteris, 2011; Babushok, 2012). This provided some possible explanations about the chemistry involved. More practical test work was requested to investigate specific properties of the subject agents and verify calculation models as existing experimental test results did not provide information relevant for the specific conditions.

1.2   Test requirements

The FAA has defined a minimum performance standard for cargo compartment protection (Reinhardt, 2012). The specific conditions of aircraft fire protection mean that the agent concentration can vary over a prolonged period of time, in which a number of fire scenarios can occur. Requirements for the performance of aviation agents can differ from what is required from suppression agents in fixed ground-based industrial systems. A test program was developed based on previous test results and research performed by the FAA and NIST. The subject of investigation was the behaviour of alternative agents at values below their established inerting concentration against various concentrations of gaseous fuel. The two agents selected for the tests were HFC-125 (C_2HF_5) and Novec™1230($C_6F_{12}O$).

2. Experimental

2.1   Test materials

The following materials were used: Propane, C_3H_8, (99.5%) supplied by BOC. Nitrogen, N_2, (99.9%) supplied by BOC. Halon 1301, CF_3Br, (Recycled: 99.6% minimum) supplied by Kidde Graviner. HFC-125, C_2HF_5, (99.9%) supplied by Kidde Aerospace. Novec™1230, $C_6F_{12}O$, (99.9%) supplied by Kidde Fire Protection.

2.2   Methodology

The test procedure was based on the European standard EN 1839:2012, method B. The test apparatus used in this program was a spherical 43 l explosion test vessel, fitted with a spark ignition unit with tungsten electrodes positioned at the centre of the vessel. The apparatus was fitted with pressure sensors and thermocouples to measure pressure rise and flame propagation during explosion tests, shown schematically in Figure 1. The positioning of the three thermocouples in the vessel in line above the ignition source gave the advantage of measuring flame propagation during explosion in the vessel, and signs of flame detachment at incomplete combustion events.

2.3   Measuring equipment

2.3.1 Pressure

The pressure was monitored with piezoresistive transducers, Kistler type 4045 A2, for low pressure (0-2 bar abs) during filling of the apparatus and type 4045 A20, for high pressure (0-20 Bar) during the explosion event. The signal from the transducers was conditioned via a Kistler type 4603 amplifier to the data acquisition equipment. The measuring accuracy of the combination was better than 1% of the full scale output.
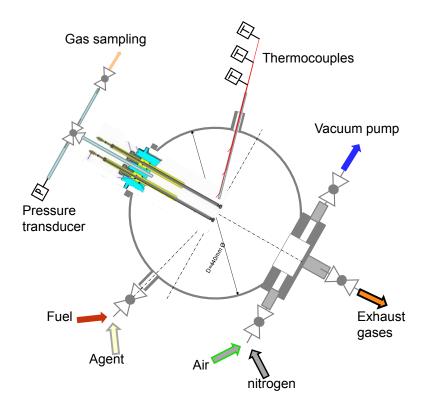
Figure 1: Schematic test vessel

2.3.2 Temperature

Internal temperature measurement was provided by three thermocouples, inserted 65 mm apart in a 6 mm stainless steel tube into the vessel. A fourth thermocouple was placed on the outside wall to monitor the skin temperature and regulate the heating. The thermocouples used were Type K; mineral insulated, metal sheathed thermocouples with 0.5 mm sheath diameter and compliant with BS EN 60584-2 with a tolerance value according class 2. The overall diameter of 0.5 mm of the thermocouples ensures a typical response time of 0.03 s to achieve a value of 63% of the actual temperature when subjected to an instantaneous step change in temperature.

2.3.3 Data acquisition

Data logging was provided by a Dell PC, Type Optiplex 780 with Dual CPUs E8500 @ 3.16 GHz, in combination with a Data Translation module DT9805. The data acquisition software was a LabVIEW derived datalogging application. During this test series the data were captured at a frequency of 1 kHz.

2.3.4 Gas composition analysis

The gases were introduced into a vacuum vessel and partial pressure was used as an indication of the volumetric percentage of the components. After filling, gas samples of the mixture were taken. The gas samples were analysed with:

- FTIR analysis, Bruker Equinox 55 Fourier Transform Infrared Spectrometer
- Oxygen analyser, Servomex Xentra 4100 paramagnetic oxygen analyser

2.3.5   Data analysis

The captured data were transferred to a self-developed MS-Excel™ spreadsheet to process and analyse the data per test. An example of data measured during an explosion test can be found in figure 2. Significant data such as explosion pressure rise (F), dP/dt, rate of pressure rise (K_g) etc. were transferred to a summary spreadsheet with the collected test results.
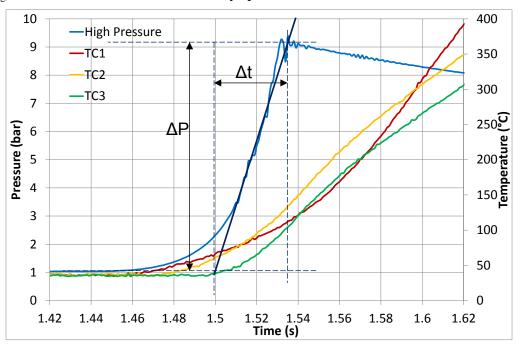

Figure 2: test result unsuppressed 4.15 vol% propane explosion

3.   Test results

Note: All points depicted in the graphs and charts showed signs of combustion, i.e. a pressure increase or heat generation more than produced by the ignition source alone.

Baseline propane air unsuppressed explosions were used to characterise and validate the test apparatus. Further validation was carried out using Halon 1301 and nitrogen, two well-known gaseous suppressants with documented inerting concentrations. Two candidate agents were then evaluated: HFC-125, and Novec 1230™. In addition, tests were carried out with mixtures of HFC-125 and nitrogen.

3.1   Validation Experiments

Baseline unsuppressed results agreed with published values. Figure 3 and 4 show graphs of the results. Inerting with nitrogen provided the limiting oxygen concentration (LOC).

Table 1, Overview propane explosion baseline data

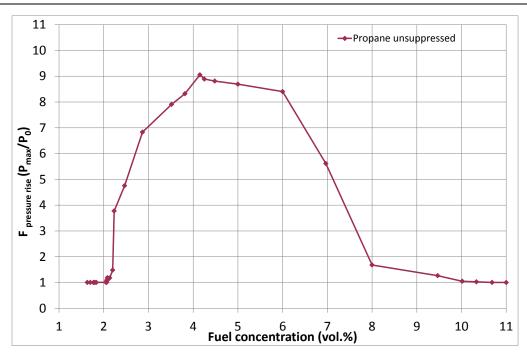| Parameter	LEL	UEL	P_{max}	K_G	LOC
Data Source	vol%	vol%	bar(abs)	bar m/s	vol% O_2
GESTIS substance database (2013)	1.7	10.8	9.4		9.8
Senecal and Beaulieu (1998)			8.2	76	
Bartknecht (1993)	2.4	8.5	8.9	100	
Kuchta (1985)	2.1	9.5			11.5
This work	**2.1**	**10.0**	**9.4**	**92**	**11.3**

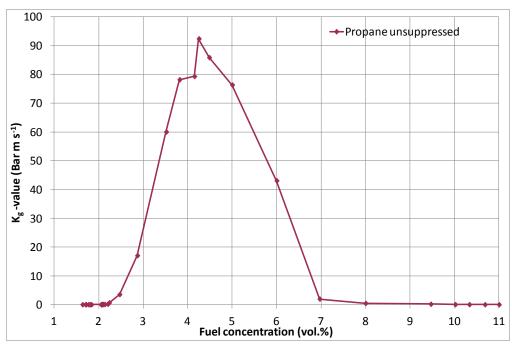Figure 3: Pressure rise (F) unsuppressed propane explosions

Figure 4: Rate of pressure rise (K_g) unsuppressed propane explosions

3.2 Tests at sub-inerting concentrations

3.2.1 Halon 1301and nitrogen

Inerting concentration Halon1301   – propane = 6.1vol% (Coll, NFPA 12A, 2004)

Inerting concentration nitrogen   – propane = 42 vol% (Zabetakis, NFPA 2001, 2004)

Halon 1301 or nitrogen when below inerting concentrations mitigated the explosion pressure in all test configurations. A combination of 2 vol% Halon 1301 and 10 or 20 vol% nitrogen resulted in enhanced suppression, as shown in figure 5.
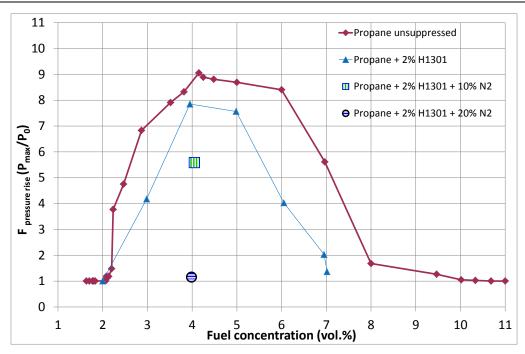
Figure 5: Pressure rise (F) partial inerting with 2 vol% Halon 1301

3.2.2   HFC-125 with propane

3.2.2.1 HFC-125 at 5%

Inerting concentration HFC-125   − propane = 15.7 vol% (Senecal, NFPA 2001, 2004)

HFC-125 was tested in a concentration of 5 vol% against propane. At fuel rich concentrations the explosion was mitigated, at fuel lean mixtures the explosion was enhanced, as shown in figure 6.
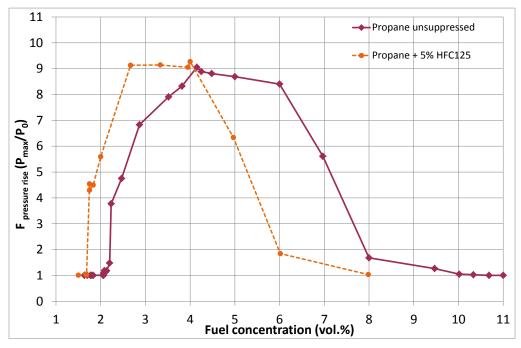

Figure 6: Pressure rise (F) partial inerting with 5 vol% HFC-125

3.2.2.2 Propane at 4% and 2%

Nitrogen and HFC-125 varying from 0.1x up to 0.9x of their full inerting concentration were tested against propane/air mixtures with 4 vol% (stoichiometric) propane and 2 vol% (2.1 vol% = Lower Explosion Limit) propane.

In the tests with 4 vol% propane, the addition of 4 - 5 vol% HFC-125 resulted in a slight increase of explosion pressure, see figure 7, but at the same time a gradual decrease in the rate of pressure rise (K_g), see figure 8. The combustion process was slowed down. It was noticed that both nitrogen and HFC-125 needed at least 0.6x of the full inerting concentration to achieve significant explosion mitigation.
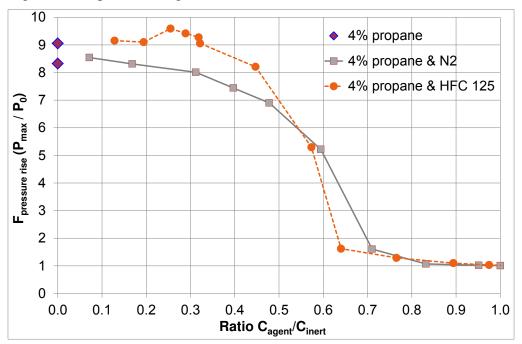
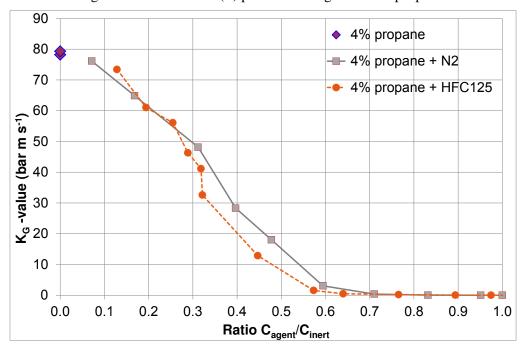Figure 7: Pressure rise (F) partial inerting of 4 vol% propane

Figure 8: Rate of pressure rise (K_g) partial inerting of 4 vol% propane

In the tests with 2 vol% propane a completely different behaviour was observed. The addition of various concentrations of HFC-125 turned a non-explosive propane/air mixture into a very reactive mixture with explosion overpressures up to 5 bar. The highest overpressures and rate of pressure rise were measured between 4 and 7 vol% HFC-125. See figure 9 and figure 10.
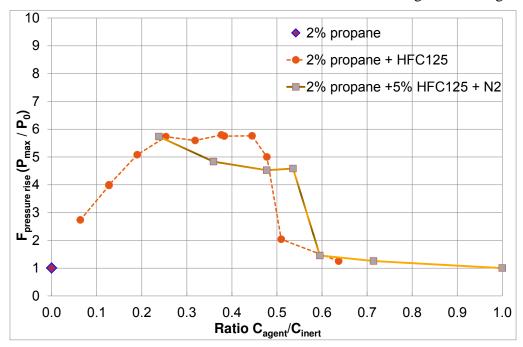

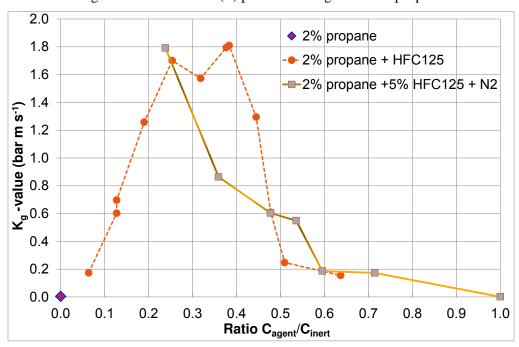Figure 9: Pressure rise (F) partial inerting of 2 vol% propane

Figure 10: Rate of pressure rise (K_g) partial inerting of 2 vol% propane

Additional tests were performed to investigate the influence of nitrogen on the explosion severity of the mixture of 2 vol% propane with 5 vol% HFC-125. Nitrogen provided again significant mitigation of the event when used in concentrations of at least 0.6x of the full inerting concentration of 42 vol%. See figure 9 and figure 10.

3.2.3 Novec™1230

Inerting concentration Novec™1230 – propane = 8.1 vol% (Schmeer, NFPA 2001, 2004)

A final test series was performed with a low concentration, 2.5 vol% Novec™1230 against propane/air mixtures at various concentrations. This showed similar behaviour to that observed with the HFC-125 tests. At rich fuel/air mixtures (above stoichiometric concentrations) the Novec™1230 mitigated the explosion pressure; at lean fuel/air mixtures the explosion severity was enhanced. See figure 11.
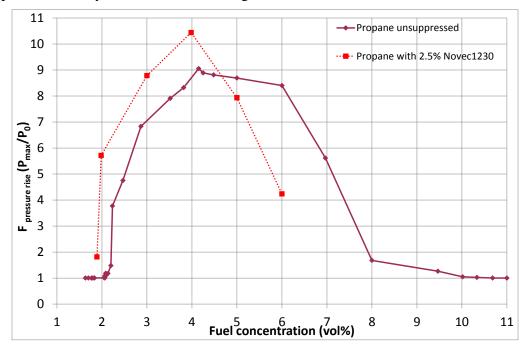

Figure 11: Pressure rise (F) partial inerting with 2.5 vol% Novec1230™

4. Discussion

The objective of this work was to develop a laboratory scale experiment to validate the theoretical work of Linteris (2011) and Babushok (2012) for aviation applications. The results of this work support their calculation model. The fire suppressing property of fluorinated agents is mainly based on heat absorption, thereby cooling the flammable mixture (Linteris, 1995). During this process the agent decomposes and the fluorine reacts with the hydrogen component of the fuel in an exothermic reaction, replacing the hydrogen-oxygen reaction with a hydrogen-fluorine reaction. Effectively this means that a low concentration hydrocarbon fuel combined with low concentration fluorine based suppression agent results in a highly reactive flammable mixture. It is important to keep this in mind during the design of a suppression system.

5. Conclusions

Normally during qualification tests for new agents, the stoichiometric concentration of a fuel is deemed to be the worst case scenario and the baseline against which agents are tested. The above described test results show that this assumption may need to be reconsidered.

In real fire scenarios fuel air mixtures are never homogeneous. This means that during discharge of alternative agents in an enclosure with flammable vapours a situation may occur where the agent enhances the fire. A critical situation may occur as well when a protected enclosure is vented after successful suppression of a fire involving a fuel rich mixture.

References

Babushok, V.I. et al. (2012). Combustion properties of halogenated fire suppressants. Combustion and Flame, 159, 12: 3569-3575

Bartknecht, W. (1993). Explosionsschutz, Grundlagen und Anwendung. Springer Verlag, Berlin Heidelberg.

EN 1839 (2012). Determination of explosion limits of gases and vapours. Technical Committee CEN/TC 305, Brussels.

Gestis Database on hazardous substances, German Social Accident Insurance, www.dguv.de/ifa/gestis-database.

Grosshandler, W.L. et al. (1994). Suppression Effectiveness of Extinguishing Agents Under Highly Dynamic Conditions. Proceedings of the 4th international symposium on Fire Safety Science, 4: 925-936.

Grosshandler, W.L. et al. (1997) Suppression of High Speed Flames and Quasi-detonations. Proceedings of the 5th international symposium on Fire Safety Science 5: 853-846.

Kuchta, J.M. (1985). Investigation of Fire and Explosion Accidents in the Chemical, Mining, and Fuel-Related Industries- A Manual. US Bureau of Mines, Bulletin 680.

Linteris, G.T. (1995) Effect of inhibitor concentration on the inhibition mechanism of fluoromethanes in premixed methane-air flames. Halon Replacements, Technology and Science, 260-274.

Linteris, G.T. Et al. (2011) Thermodynamic Analysis of Suppressant-Enhanced Overpressure in the FAA Aerosol Can Simulator. Proceedings of the 10th international symposium on Fire Safety Science, 10; 307-320.

NFPA 12A (2004). Halon 1301 Fire Extinguishing Systems. National Fire Protection Association, Batterymarch Park, Quincy, MA.

NFPA 2001 (2004). Clean Agent Fire Extinguishing Systems. National Fire Protection Association, Batterymarch Park, Quincy, MA.

Reinhardt, J.W. (2004). Behaviour of Bromotrifluoropropene and Pentafluoroethane When Subjected to a Simulated Aerosol Can Explosion. DOT/FAA/AR-TN04/04 National Technical Information Service (NTIS), Springfield.

Reinhardt, J.W. (2012). Minimum Performance Standard for Aircraft Cargo Compartment Halon Replacement Fire Suppression Systems (2012 Update). DOT/FAA/TC-TN12/11 National Technical Information Service, Springfield.

Senecal, J.A. & Beaulieu, P.A. (1998). Kg: New data and analysis. Process Safety Progress, 17(1): 9-15.