FIRE SUPPRESSION AND INERTION TESTING OF HALON 1301 REPLACEMENT AGENTS

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INTRODUCTION

Enclosed areas containing flammable hydrocarbon fuels and gases present challenging fire and explosion protection problems. Of particular concern are Alaskan North Slope petroleum handling facilities (Ref. 1), where leaks of flammable gaseous and liquid hydrocarbons can occur. The current fire and explosion protection measure for such facilities is total-flood application of Halon 1301; however, due to adverse environmental impacts and resultant regulations, the availability of halon fire extinguishing agents (e.g., Halon 1301) will decrease substantially. This paper presents results from a study of the potential use of perfluorocarbon (FC) and selected hydrofluorocarbon (HFC) and hydrochlorofluorocarbon (HCFC) chemicals as Halon 1301 replacements for total-flood applications at North Slope facilities. Agents were ranked according to the liquid storage volume required to provide the same inertion performance as Halon 1301.

A list of candidate agents has been developed (Table 1), which have been tested at laboratory scale, in the NMERI 5/8-scale cup burner test, to determine their effectiveness in suppressing liquid hydrocarbon flames (Ref. 2). An explosion sphere apparatus was designed and constructed to measure the inertion ability of selected candidates and to determine a relative ranking of performance among candidates. A flammable mixture was considered inert if the overpressure due to the explosion of the hydrocarbon was limited to 1 psi or less. The concentration of each candidate agent at which that occurs is called the minimum safe inerting concentration (MSIC).

FLAME SUPPRESSION TESTING

While the goal of this program was to determine optimum agents to prevent explosions in a flammable environment, it is also important that any candidate agent be able to extinguish a fire. The recognized laboratory-scale fire suppression test method is the cup burner apparatus.

Table 1. Cupburner And Inertion Results.

Agent	Formula	**Extinguishment** Concentration **(NMERI** Cupburner) Gas Vel. %	Propane MSIC Gas Vol. %	Propane SVEq	Propane SVEq Rank	Methane MSIC Gas Vol. %	Methane SVEq	Methane SVEq Rank
1301	$CBrF_3$	2.9	4.3	1.0	-	4.3	1.0	-
1311	CF_3I	3.0	5.1	0.99	1	3.1	0.60	1
14	CF_4	13.8	21.0	3.29	11	18.0	2.79	13
22	$CHClF_2$	11.6	18.8	3.19	9	14.6	2.49	12
22B1	$CHBrF_2$	4.4	8.0	1.58	3	5.6	1.11	4
23	CHF_3	12.4	19.8	4.85	18	14.0	3.43	16
32	CH_2F_2	8.8	17.5	2.18	5			**Not** *tested*
116	CF_3CF_3	7.8	15.7	3.19	10	10.1	2.05	7
124	$CHClFCF_3$	8.2	12.0	2.80	8	9.1	2.09	9
124B1	CF_3CHFB_3	2.8	5.6	1.28	2	3.6	0.83	2
125	CHF_2CF_3	9.4	14.7	3.30	12	9.7	2.18	10
134	CHF_2CHF_2	11.2	14.0	2.79	7			**Not tested**
134a	CH_2FCF_3	10.5	13.5	2.68	6	7.8	1.56	6
142b	$CClF_2CH_3$	11.0 (Calc)	19.3	4.05	17	5.4	1.13	5
152a	CHF_2CH_3	27.0 (Calc)	10.0	1.70	4	6.5	1.11	3
218	$CF_3CF_2CF_3$	6.1	11.2	3.65	15	8.9	2.06	8
227ea	CF_3CHFCF_3	6.6	12.0	3.37	13	8.0	2.25	11
C318	C_4F_8	7.3	11.6	3.67	16	8.9	2.82	14
PFC410	C_4F_{10}	5.5	9.5	3.48	14	7.8	2.86	16

INERTION TESTING

Test Apparatus

The explosion sphere was modeled ***after*** the Fenwal Explosive Sphere (Ref. 3). It consisted of two **25-cm (9-3/4** inch) 304-stainless steel hemispheres welded **on** stainless steel flanges which could be fastened to form a sphere with a **measured** volume of 7930 cubic centimeters (Figure **1).**

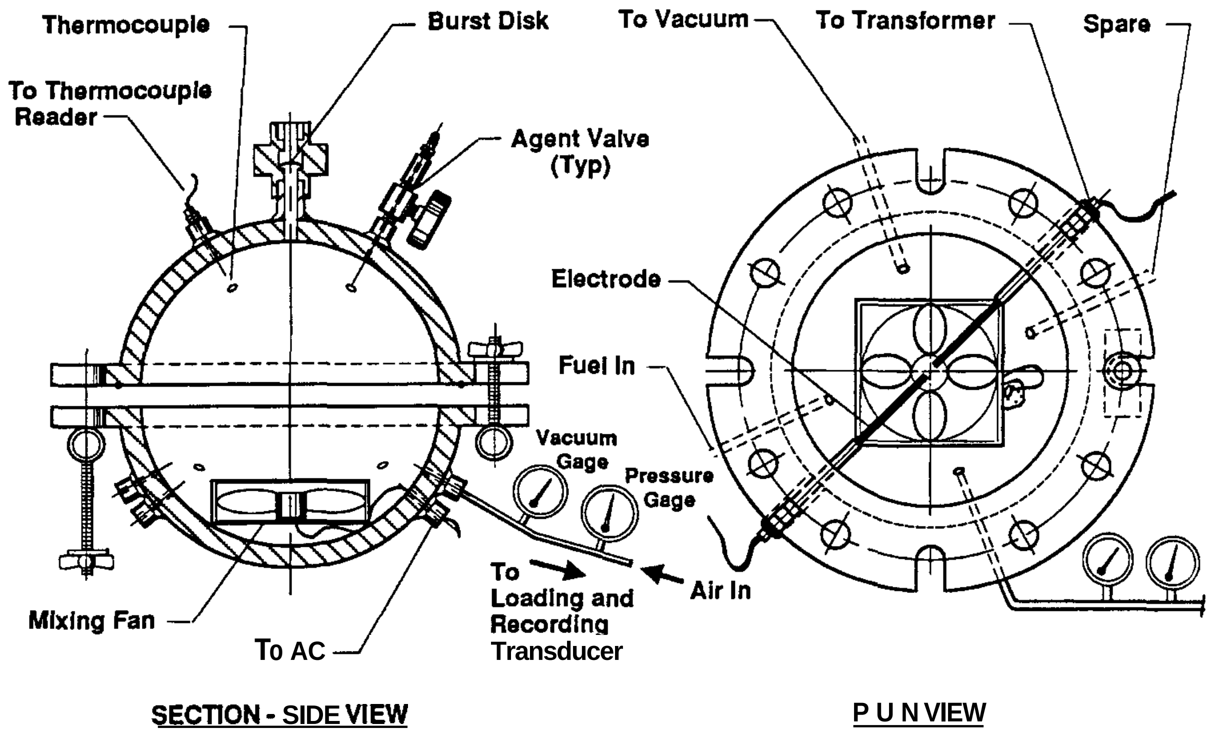

Figure 1. NMERI Explosion Sphere

A **mixture** of fuel and air and the desired concentration of inerting agent were introduced in the sphere using the partial pressure method to determine the correct volumes of agent, fuel, and air. The loading pressure was measured by a 0 to 2.5 psi transducer. A fan internal to the sphere provided **mixing.** The *mixture* was ignited by a variable power DC spark generated between electrodes located in the center of the sphere. The resulting overpressure was detected by a 0 to 50 psi pressure transducer and the pulse recorded on a Hewlett-Packard data acquisition system (H-P DAS). Overpressure relief was provided by a 3/4-inch safety vent disc installed in a rupture disc holder on top of the sphere. Pipe nipple penetrations provided the inlets for the fuel, air, and agent, pressure transducer openings, and the vacuum and exhaust **port,** as well as the thermocouple and fan power penetrations.

Data acquisition and recording, as well as the charging of the capacitors, was automatically controlled through a Hewlett-Packard Data Acquisition System (**H-P** DAS). The system controller was an **H-P** 86B computer which monitored the system operation and the partial pressures of the agent, fuel, and air during the loading process, and recorded the pressure pulse data. Test data was stored on 3-1/2 inch floppy disks.

Test Procedures

Tests were conducted at the NMERI/CGET Chemistry Laboratory. The apparatus was contained in a fume hood, with exhaust gases passing through a cryotrap before being released to the environment. To begin testing, the H-P DAS was turned on, the computer program loaded, and test information entered. All testing was performed at a pressure corresponding to sea level (about 2.6 psi above the normal ambient pressure in Albuquerque). To ensure repeatability and simplify calculations, a correction from local atmospheric pressure to sea level was determined at least twice per test day. The transducer amplifier gain and excitation voltage were measured and recorded. The agent to be tested was connected to the upper pipe penetration. The correct amounts of agent, fuel, and air were calculated for the required percentage of agent according to the partial pressures method. A monitor next to the sphere displayed a readout of the sphere internal pressure and the desired partial pressure of agent, fuel, and air. The operator added the components to the required loading pressures by controlling the input valves on the sphere.

After all components were loaded into the sphere, the mixing fan was turned on for one minute (propane) or two minutes (methane) to ensure that the components were completely mixed. The internal sphere temperature was recorded and the desired spark energy was entered into the computer. The capacitors were charged. A push button discharged the capacitors across the electrodes, the explosion (if any) occurred, and the pressure pulse was recorded. The computer calculated pressure data from the voltage data Both voltage and pressure results were stored on a 3-1/2 inch disk, and results were plotted or printed as desired. After each test, a plot of explosion overpressure vs. time was generated, and the maximum overpressure determined. Plots of the maximum overpressure vs. concentration were drawn and tests continued until at least one test resulted in an overpressure of 1 psi or less. The MSIC was taken as the concentration where the overpressure curve passed through 1 psi or where no further explosion occurred.

Test Matrix

Calibration and Baseline Testing. The primary purpose of this series was to determine optimum test conditions, with regard to the energy of the ignition spark and fuel-to-air ratio, to develop baseline Halon 1301 data for comparison with data from other research to ensure that results from this testing are comparable to other efforts, and to provide a reference for replacement agent testing.

Agent Screening. After completion of the calibration and baseline Halon 1301 testing, the process of screening large numbers of agents was begun. The required inertion concentration for each agent was estimated based on a ratio of its cup burner extinguishment concentration to that of Halon 1301. The initial test was run at this concentration and the concentration was increased or decreased based on the resultant overpressure. Sufficient tests were run to draw a curve of peak overpressure vs. concentration such that the concentration required to reduce the overpressure to 1 psi could be determined. Several brominated and iodinated candidates identified in the expanded scope of work for the project were tested as a preliminary indication of performance for these families of halocarbons.

Blending. Because of the outstanding performance of iodinated and brominated agents, it was decided to blend minor percentages (up to 15% of the agent amount, or 2% of the total volume) of them with several agents which exhibited moderate inertion capability as well as offering good cost, availability, and toxicity tradeoffs. Agents were added to the sphere in the correct partial pressures to give the desired percentages of major and minor components. Also, since two high hydrogen content agents performed better than expected, it was also decided to blend these agents - HFC-152a and HCFC-142b - to determine their impact in a blend.

Three agents were utilized as the major components - PFC-410, HFC-134a, and HFC-32 - and five as minor components - Halon 1301, FIC-1311, HBFC-124B1, HFC-152a, and HCFC-142b. In addition, equal amounts of FIC-1311 and HBFC-124B1 were substituted as the minor blend to determine the combined effect of brominated and iodinated agents (Table 2). Note that the total agent percentage represents the total amount of agent, both major and minor components, used. The minor component percentage represents that percentage of the previous amount which is a minor component. For example, if the total agent percentage is 7% and the minor component percentage is 5%, the agent concentration is 7% of which 95% (or 6.65% of the total) is the major component and 5% (or .35% of the total) is the minor component, Where two minor components were used, the percentage of each is noted.

INERTION RESULTS

Calibration and Baseline Testing

Fuel-to-air Ratio. A stoichiometric fuel-to-air ratio produced a mean overpressure of 94.5 psi. For the 24 tests in which the mixture was within plus or minus 6% of stoichiometric, the mean maximum overpressure was 93.7 psi. Therefore, while the stoichiometric ratio produced the greatest overpressure, any fuel-to-air ratio between plus or minus 6% of stoichiomemc produced statistically the same overpressure. When fuel-to-air ratios were kept within ± 6% of stoichiometric, consistent test results were observed.

Table 2. Blend Inertion Data.

		Methane			Propane		
Maja Change Component	Minor Component(s)	MSIC of Mixture Gas Vol. %	SVEq of Mixture	% Change In SVEq	MSIC of Mixture Gas Vol. %	SVEq of Mixture	% In SVEq
PFC-410	None	7.8	2.86				
	1301	5.7	1.97	-31			
	124B1	5.1	1.77	-38			
	152a	7.8	2.63	-8			
134a	None	7.8	1.56		13.5	2.68	
	124B1				9.9	2.02	-25
	1311	5.13	1.01	-35	10.3	2.05	-23
	124B1/1311[2]				9.7	1.96	-27
	142b	7.2	1.45	-7	13.3	2.68	0
	152a	7.2	1.40	-10	13.8	2.70	0
32	None				17.5	2.18	
	1311				13.0	1.72	-21

1 Minor blends are 15% of total agent amount except where noted.
2 7.5% 124B1 - 7.5% 1311 for propane.
3 10% concentration of minor agent.

Spark Energy. Of the **24** tests meeting the above fuel-to-air ratio criteria, **11** were run at **100** Joules, **3** at **90**, **7** at **70** Joules and **2** at **40** Joules. The mean maximum overpressures with respect to spark energy were as follows: for **100** Joules, the mean maximum overpressure was **94.90** psi; for **90** Joules, **93.33** psi; for **70** Joules, **92.37** psi; and for 40 Joules, **93.35** psi. Since the differences between the four energy levels varied by less than **2.7%**, it was decided to test at **70** Joules.

A brief series using propane as the fuel was conducted which confirmed that the results seen with methane could be extended to propane. Ten tests run at **70** Joules indicated that those run at a stoichiometric fuel-to-air ratio resulted in a mean maximum overpressure of **103.85** psi, while those within plus or minus **6%** resulted in a mean maximum overpressure of **104.17** psi.

Halon 1301 Testing. Fifty-two tests were run to determine the **MSIC** of Halon **1301** with propane. Twenty tests were run to determine the **MSIC** for methane. The **MSIC** for Halon **1301** using both methane and propane for a fuel was **4.3%**, rounded to the nearest tenth of a percent.

Agent Screening

Twenty-three agents were tested in this series, the majority of candidates being tested using both propane and methane separately as a fuel. The **MSIC** was defined as either the concentration at which the curve of peak overpressure vs. concentration passed through **1** psi overpressure or the first concentration resulting in 0 psi. Agent **MSICs** for propane and methane **are** presented in Table 1.

Several agents from the expanded scope of work were added to the test matrix. Based on low cup burner fire suppression concentrations, two agents - **FIC-1311** and **HBFC-124B1** - were included even though toxicity and **ODP** concerns remained. **HBFC-22B1** was included to investigate the effects of bromine and because it is commercially available in bulk. **CFC-12** and **CFC-114** were included to provide a comparison between **CFCs** and current candidates, and **PFCs-512, -614,** and **-716,** became available for testing during the program, but were not analyzed in this phase.

Blending

Results from blends **are** shown in Table **2.** Where adequate data points were available, the **MSIC** was calculated as in the single component tests. Where only one point was available, a curve with the same slope as the major component was drawn through that point, and the MSIC determined at the intersection of the 1 psi line.

INERTION ANALYSIS

Agent Screening

Inertion results are usually given as the minimum gas-phase concentration needed to inert a flammable mixture. This can be related to a reference compound (usually Halon 1301) to calculate a Gas Volume Equivalent (GVEq). For example, if a candidate agent has a MSIC defined as $MSIC_C$ and a reference compound has a MSIC defined as $MSIC_R$, then the Gas Volume Equivalent is given by Equation (1).

$$GVEq = MSIC_C/MSIC_R \qquad (1)$$

Note that the GVEq gives the increase in gaseous volume of a candidate agent needed to provide inertion as measured by an inertion equivalent to the reference agent.

The gas-phase concentration of an agent required to inert a mixture is not always a good measure of agent efficiency. The weight and storage volume of an agent required to give the same inertion capability as a reference compound are more critical when agents are considered for real world usage such as in the North Slope application. The Weight Equivalent (WEq) is the ratio of the weight of the candidate agent relative to the weight of the reference agent. The equation used is

$$WEq = GVEq \times (MW_C/MW_R) = (MSIC_C/MSIC_R) \times (MW_C/MW_R) \qquad (2)$$

where, "MW" denotes "molecular weight," the subscript "C" denotes "candidate," and the subscript "R" denotes "reference agent" Note that as the molecular weight of the candidate agent increases, the Weight Equivalent increases. Thus, lower molecular weight materials appear to be more effective when effectiveness is measured by weight Like the numbers for gas volume, a higher efficiency is denoted by a lower WEq.

The Storage Volume Equivalent (SVEq) is the amount of candidate agent as measured by storage volume requirements relative to that required by a reference agent. The storage density of the agent is important in determining the storage volume requirements. A higher density means that less space is required. Since most agents of interest here *are* stored as liquids, usually under pressure, the liquid densities (LD) *are* used to determine the **SVEq** (Equation (3).

$$SVEq = WEq \times (LD_R/LD_C) = (MSIC_C/MSIC_R) \times (MW_C/MW_R) \times (LD_R/LD_C) \quad (3)$$

Blends

The **SVEq** of the blends was calculated based on the MSIC of the total mixture, the relative propomon of major and minor components, and the molecular weights and liquid densities of the components. Results **are** presented in Table **2.**

DISCUSSION

Halon 1301

The value of 4.3% minimum inemng concentration for both propane and methane contrasts with the results reported by Fenwal in Reference **2** of a MSIC of *6%* for propane and **7%** for methane. For all candidate replacement agents tested, only two CFCs, (-12 and -114), required less agent to **inert** propane than methane. **Since** the measure of performance of replacement agents is a comparison to Halon 1301, an understanding of the differences between the two studies is critical. It is important to understand how differences in test equipment and techniques could lead to significant differences in the MSICs. Several potential explanations of the discrepancies between current test results and the results from Reference **2** *are* presented below.

Mixing. Fenwal loaded the sphere with agent and fuel from a vacuum, and mixed the components as the air entered the chamber, returning the mixture to atmospheric. This test program determined that the fan had to **run** for either one or two minutes to achieve acceptable test result repeatability.

Cleaning. Fenwal indicated that in all tests resulting in a pressure increase, the vessel was opened and cleaned by wiping with a clean cloth and blowing away residue with **air.** After all other tests, the sphere was evacuated and air introduced to clean the sphere. **Our** test program determined that the sphere had to be opened and cleaned with acetone between every test, and opened and cleaned with compressed **air** if the test was aborted during the **loading** process.

Ignition Source. Differences between the type of ignition source are the most likely causes for the discrepancies between our results and Fenwal's. The current testing discharged the spark in a 6 mm air gap between two electrodes, while Fenwal connected the electrodes with graphite, apparently vaporizing the graphite as the current was applied. Fenwal used 11 Joules for their some; our testing used 70 Joules, which according to our analysis and results should be well above the minimum required to be insensitive to spark energy.

Agent Testing

The purpose of this study was to identify candidate agents with low **ODPs** having a potential to replace Halon 1301 in North Slope fire and explosion protection applications. A requirement of any replacement agent is that the amount of additional storage required above that of Halon 1301 be minimized. It has been demonstrated that the worst case environment is propane; therefore the ranking criteria that will be used is the Storage Volume Equivalent (SVEq) for propane presented in Table 1. Those agents with the lowest SVEq will be tested at a larger scale.

No candidate except for those containing bromine or iodine has a SVEq of less than 1.70. HFC-152a is a high hydrogen content agent which may make it unsuitable for use as a fire suppression or inertion agent. HFC-32 has the next lowest SVEq at 2.18 followed by HFCs -134 and -134a and HCFC-124, which have SVEqs of nearly 3.

FIC-1311 performed as well as Halon 1301 on a storage volume basis. However, the liquid density has only been reported at -42 °C. If the density decreases considerably as room temperature is approached, its storage volume equivalent will increase. Nonetheless, the good performance of FIC-13I1 as well as HBFCs-22B1 and -124B1 make them attractive for potential replacements. If ozone depletion and global warming potentials are acceptable, or if they could be blended them with an agent to reduce values to acceptable levels, they offer great potential for this use.

Blending

Small amounts of brominated or iodinated agents added to major components can result in a mixture which has a SVEq in the vicinity of 2.0. However, only a limited number of tests were performed with blends and potential agent compatibility and storage obstacles may prevent blended agents from being practical. Also, several concerns still exist about the logistics of using a blend in a total flood situation.

CONCLUSIONS AND RECOMMENDATIONS

The results obtained from this testing represent laboratory-scale testing within controlled parameters. **Care** must be taken not to extrapolate results to larger scale. Any agent chosen for this application must be able to be stored for long periods of time under severe temperature conditions. It must be able to be rapidly dispersed throughout the volume to be inerted and must have a hold time of at least 30 minutes. While most of the agents tested appear to have acceptable toxicity, extensive research must be undertaken **prior** to deployment of the agent. Compatibility with materials both in the inemon system and equipment located throughout the volume to be inerted must be assured.

It is recommended that the following agents be tested in larger scale inemon tests: HFCs-32, -134a, and -152a and HCFC 124. At present, taking into consideration pexfornance, availability, and toxicity, these agents offer the best compromise for a near-tern solution. All, except for HFC-32 and HCFC-124, which **are** becoming more available, are produced in bulk. Environmental and toxicity concerns surrounding FIC-1311 and HBFC-124B1 should be further investigated. If these agents meet the selection criteria, they should also be included in larger scale testing, either alone or **as** part of a blend.

ACKNOWLEDGMENT

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