Determination of Suppression Concentration for Clean Agents Exposed to a Continuously-Energized Heated Metal Surface'

Emil Braun, Carole Womeldorf, and William L. Grosshandler

National Institute of Standards and Technology
Building and Fire Research Laboratory
Building 224 Room B356
Gaithersburg, MD 20899

Abstract

The National Fire Protection Association (NFPA) standard on clean agent fire extinguishing systems, NFPA 2001, was developed in response to international restrictions on the production and use of certain halon fire extinguishing agents. The standard addresses minimum requirements for total flooding clean agent fire extinguishing systems. The amount of agent necessary to suppress the fire is estimated from the result of cup burner tests assuming total gasification of agent and uniform distribution throughout the enclosure. NFPA 2001 is applied to Class A, B, and C types of fire. A basic assumption of NFPA 2001, with regard to Class C type fires is that agent concentration requirements are comparable to Class A and B type fires.

In an effort to quantify the effectiveness of various agents to suppress ignition or reignition in the presence of hot surfaces, an apparatus for determination of autoignition temperature of hydrocarbon fuels was used to measure the change in ignition temperature of a stoichiometric mixture of ethene-air with and without the addition of various concentrations of agent. Six agents were selected for evaluation -- N_2, INERGEN (54% N_2, 40% Ar, 8% CO_2), HFC-23, HFC-227ea, FC-218, and FC-3-1-10.

When exposed to a heated metal surface of nickel, the ignition temperature of a stoichiometric mixture of ethene-air was found to be $750 \pm 34°C$. In general, the addition of a clean agent in the fuel-air stream required higher nickel foil surface temperatures than the reference case. It was found that for some agents (HFC-227ea and FC-3-1-10) at low concentrations ignition became easier, i.e., lower ignition temperature. As agent concentration was increased, ignition became harder, i.e., higher ignition temperature. For this set of suppressants, the concentration of agent (volume basis) necessary to prevent ignition of the ethene-air mixture was 1.1 to 5.9 times greater than that found with the cup burner apparatus for foil temperatures approaching 1000°C.

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1. Introduction

The National Fire Protection Association (NFPA) standard on clean agent fire extinguishing systems, **NFPA** 2001 [1], was developed in response to the international restrictions on the production and use of certain halon fire extinguishing agents. The standard addresses minimum requirements for total flooding clean agent fire extinguishing systems. The amount of agent necessary to suppress the fire **is** estimated assuming the agent is totally gasified and uniformily distributed throughout the entire enclosure. **A** cup burner apparatus is normally **used** to establish the minimum effective concentration. This value **is** multiplied by a *safety* factor to account for nonuniform distribution and leakage of agent from the enclosure. **NFPA** 2001 defines effective agent concentration for clean agents based on cup burner concentration plus 20% **as** the design concentration for clean agent fire extinguishing systems for both **Class A** fires (agent concentration for solid surface fires are determined by a listing program plus 20%) and **Class** B fires (flammable liquid fires).

Class C fires are fires that involve energized electrical equipment where the nonconductivity of the extinguishing agent is of importance. **NFPA** 2001 does not define any additional factors that must be considered in determining effective agent concentration under conditions where energized electrical equipment can not be disconnected from electrical sources -- prior to, during, or after release of agent. By implication, **NFPA** 2001 applies the same agent concentrations to **Class** C fires as defined for Class **A** or B fires, because it is assumed that electrical power can normally be disconnected prior to discharge, or, if not, that the energized state does not impact the design concentration of agent needed to suppress the fire.

A series of fire suppression tests were conducted by **3M** to ascertain the effect of an electrically energized wire on the concentration of agent needed to extinguish solid and liquid fuel flames [2]. In one experiment, a bare electrical wire was placed above the liquid surface of a cup burner apparatus. Three different alternative agents, with halon 1301 as a baseline, were added to the air stream and the minimum extinguishment concentration was recorded for each at several different electrical power settings. **A** clear trend between increasing electrical power and the minimum extinguishment concentration showed that **as** much as twice the published cup burner concentration of agent was necessary to extinguish the **cup** burner flame at the highest electrical current level tested. In a second experimental setup, nichrome wire was wrapped around or placed through blocks of PMMA fuel specimens. **A** similar increase in agent concentration

needed to suppress the fire was noted in these experiments. In general, higher electrical power led to greater extinguishing agent concentration levels needed to extinguish the fire.

In an effort to quantify the effectiveness of various agents to suppress ignition, Hamins and Borthwick [3] determined the impact of fire suppressants on the possible ignition of reactants flowing over a hot metal surface. They measured the changes in ignition temperature of stoichiometric mixtures of methandair, ethene/air and propandair as a function of agent concentration for five selected agents. Their primary emphasis was on the re-ignition problem associated with the use of a fire suppressant in the vicinity of hot surfaces. The basic scenario involved the initial release of agent and the suppression of the fire. Because of the presence of fuel vapor and a hot surface, a flammable mixture may still exist that could lead to reignition. They found that conditions leading to reignition are controlled by the time/temperature history of the reactive mixture and to a lesser extent by the type of metal surface and chemical composition of the fuel.

Expanding on the work of Hamins and Borthwick, the current study investigates the use of a short-duration auto-ignition apparatus [4] to quantify the effectiveness of six clean agents in preventing the ignition of a stoichiometric mixture of ethendair, simulating the "reignition" phenomenon. Use of a gaseous fuel represents a most dangerous case, i.e., when a liquid fuel or polymeric material has completely vaporized. Ethene was used as the fuel because Symth and Bryner [4] found ethendair mixtures to have the lowest auto-ignition temperature of the alkenes and alkanes tested.

2. Materials

The behavior of six clean agents were examined under conditions simulating an electrically energized fire scenario. These six agents are listed in Table 1 along with several important physical properties: molecular weight, vapor pressure at **25** °C, heat capacity, and cup burner concentration . Two agents, N_2 and IG-541 (INERGEN' (52% N,, 40% Ar, 8% CO_2)), are inert

gas agents, i.e., diluents. The other four agents are fluorocarbons: HFC-23, HFC-227ea, FC-

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Table I. Selected properties of clean agents 161						
Property	N_2	INERGEN	CHF_3	C_3HF_7	C_3F_8	C_4F_{10}
NFPA 2001 Designation	Nitrogen	IG-541	HFC-23	HFC-227ea	FC-218	FC-3-1-10
Molecular Weight (g/mole)	28.0	48.6	70.0	170.0	188.0	238.0
Vapor Pressure at 25 °C (MPa)	14.48'	15.20*[1]	4.73[1]	0.46	0.88[7]	0.29
Specific Heat Capacity (J/g-°C)	1.041[8]	0.574[1]	0.737[1]	0.808[1]	0.794[7]	0.804[1]

* Cylinder Pressure

218, and FC-3-1-10. NFPA 2001 classifies these agents as halocarbon agents. All agents have previously been considered for class A and B applications and are nonconducting making them suitable for Class C applications.

3. Experimental Method

Tests were conducted using a short-duration auto-ignition temperature apparatus developed in a previous study [4]. Figure 1 is a schematic diagram of the experimental apparatus. The apparatus consists of the following: a premixed flame burner assembly; mass flow controllers for fuel, air, and agent; foil holder assembly; DC power supply; and a data acquisition system.

The premixed flame burner assembly consists of a mixing chamber to ensure complete mixing of fuel, air, and agent, and a burner head designed to prevent flashback upon ignition. A 22 mm long by 11 mm diameter quartz chimney is placed on top of the burner head to isolate the fuel-air-agent gas stream from the ambient air until the flow is within 6.4 mm of the hot surface. The fuel, air and agent flow is controlled by a set of calibrated mass flow controllers. The fuel, ethene, and air mixture was adjusted to maintain a constant stoichiometric ratio, $\Phi=1.0$, for all concentrations of agent. The average gaseous flow velocity exiting the quartz tube is fixed at 160 mm/s. The burner is positioned such that the initial fuel-air-agent contact point on the foil surface is in the vicinity of the lower thermocouple. The foil holder assembly is designed to allow for metal expansion during heating and to maintain contact between the foil and electrical source and two

subminiature thermocouples. The nickel metal foil used in these experiments was 0.013 mm thick and cut to an overall size of 24.1 x 101.6mm. The metal foil is cut, notched and folded as described in [4] to ensure that the maximum foil temperature occurs in the center region of the foil surface. The shiny side of the foil is exposed to the fuel-air-agent mixture and the reverse side is in contact with the two thermocouples. The holder assembly is positioned over the burner assembly at a 45° approach angle of the fuel-air-agent mixture. This results in a maximum contact (residence) time of approximately 100ms. The subminiature sheathed chromel-alumel thermocouple probes are located **1.6 nun** from the upper edge of the metal foil and **3.2 nun** from the folded lower edge of the foil. Power to the nickel metal foil is provided by a pair of 20 volt power supplies wired in parallel to provide a maximum current flow of 40 amps -- this is capable of heating the foil up to 1000°C. The data acquisition system collected data from the two thermocouples and controlled the mass flow controllers.

Bottled gases of fuel, 99.5% pure ethene, and air were used. Agents were obtained from suppliers in standard cylinders unique to each agent. Regulators and shutoff valves were added as necessary to match cylinder connections to mass flow controllers.

A new foil was used with each agent. After mounting of the metal foil, it was annealled at temperatures up to 1000°C. With each new foil, experiments were conducted first without agent, using only ethene-air. Subsequent experiments were performed with increasing concentrations of fire suppressant agent. The measurement process with or without agent was repeated three to five times to assure reproducible results. It has previously been shown that uncertainty in the measurement process was estimated to be no better than 11"C [3] based on a propagation of error analysis. Smyth and Bryner [4] found ignition temperatures of pure ethene fuel-air mixtures using nickel foil to vary ±24°C.

4. Results

Experiments were performed to determine the temperature of the hot metal surface at ignition in the presence and absence of clean fire suppressant agents. For a chosen agent mole fraction, the fuel-air-agent mixture flowed over the electrically heated metal foil and the foil temperature was increased until flames were visible or until the foil temperature reached 1000°C.

Because metal foil positioning and tensioning could affect the measured foil temperature, baseline ethene-air mixture experiments were conducted prior to the addition of any agent. The measured

ignition temperature for ethene-air mixture represented the baseline temperature for each set of experiments. The data for each agent are presented **as** a temperature change relative to ethene-air mixture ignition temperature for that set of experiments and for different agent concentrations. Replicate tests showed measurement errors that were sometimes greater than the differences between adjacent values. However, a distinction could be made between active flaming and no ignition away from the foil surface. Each data point in the figures represent the average of three to five replicates. Data points labeled **as** no ignition are effectively single deteriminations. At high agent concentrations, a distinct ignition event was difficult to define. The presence of random flashes, flickering, and glowing in the gas phase near or attached to the heated nickel foil was taken **as** an ignition event. Therefore, "no ignition" implies the absence of any indication of combustion. The average ethene-air ignition temperature at stoichiometric conditions for all tests was found to be $750 \pm 34°C$. This compares with that found by Smyth and Bryner [4], $803 \pm 24°C$, and by Hamins and Brothwick [3], $760 \pm 11°C$. While measurement uncertainty was a function of agent and agent volume fraction, it was generally found to be on the same order of magnitude as the measurement uncertainty observed with only the ethene-air mixture.

4.1 Inert Gas Agents

Two substances were tested that NFFA 2001 classifies as inert agents -- nitrogen, N_2, and INERGEN (IG-541), a mixture of N_2 **(52%),** Ar **(40%),** and CO, (8%). Figure 2 shows the effect of increasing agent concentration for N_2 and IG-541 on the ignition temperature of a stoichiometric mixture of ethene-air. The increase in ignition temperature for N_2 and IG-541 is approximately 70°C and 30°C, respectively, above the baseline ignition temperature for agent volume fraction between 0.10 and 0.40. As the agent volume fraction was increased, the position of the ignition moved from the top of the burner tubes at an agent volume fraction of 0.10 to the surface of the heated nickel foil at an agent volume fraction of 0.40. At agent volume fractions of 0.50 for N_2 and 0.55 for IG-541, no visible flames were observed at the maximum foil temperature. This is indicated by an up-arrow attached to the symbol.

4.2 Halocarbon Agents

Four halocarbon agents were evaluated -- HFC-23 (CHF_3), HFC-227ea (C_3HF_7), FC-218 (C_3F_8), and FC-3-1-10 (C_4F_{10}). In general, as agent concentrations were increased, the position of the flame at ignition migrated to the foil surface until a concentration was reached where no visible
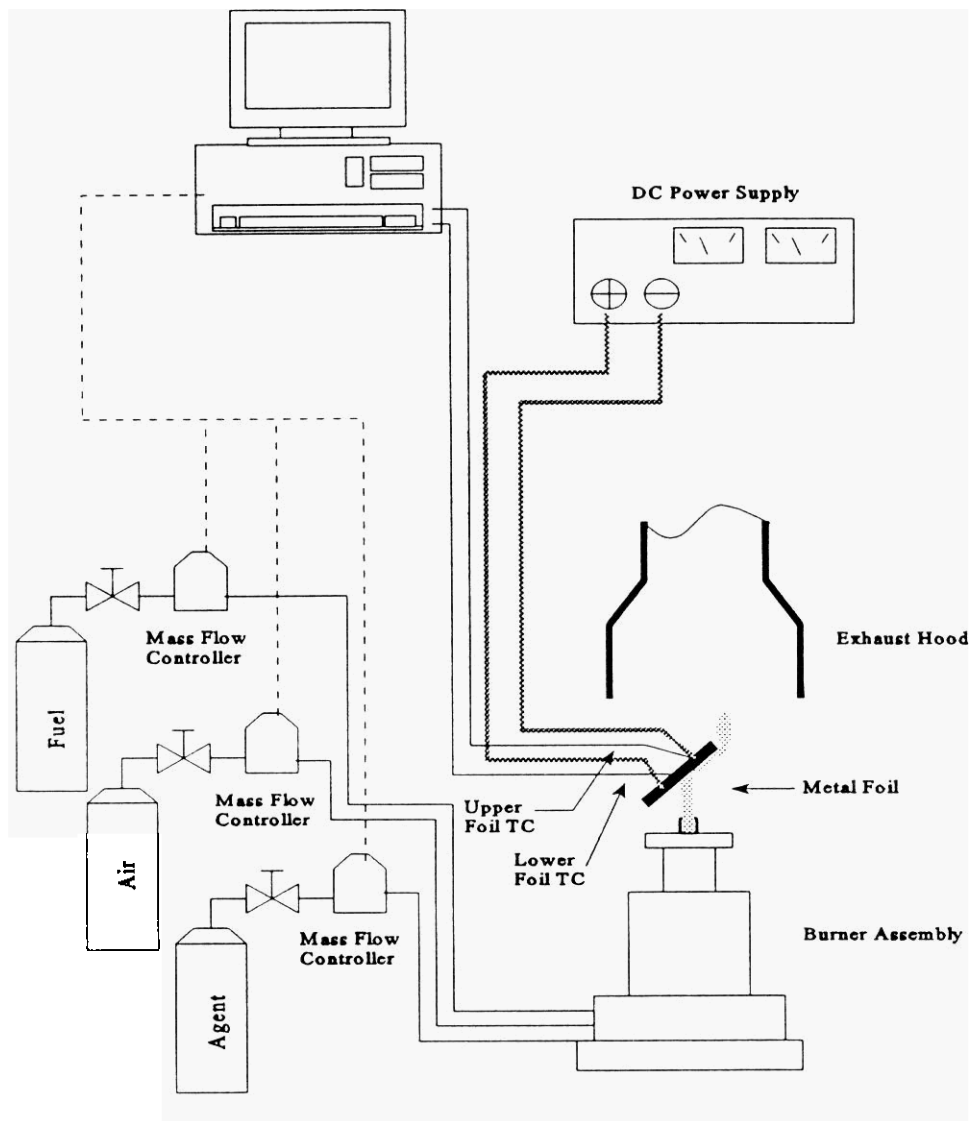
Figure 1 Schematic drawing of apparatus **used** to determine ignition temperature of fuel-air-agent mixtures
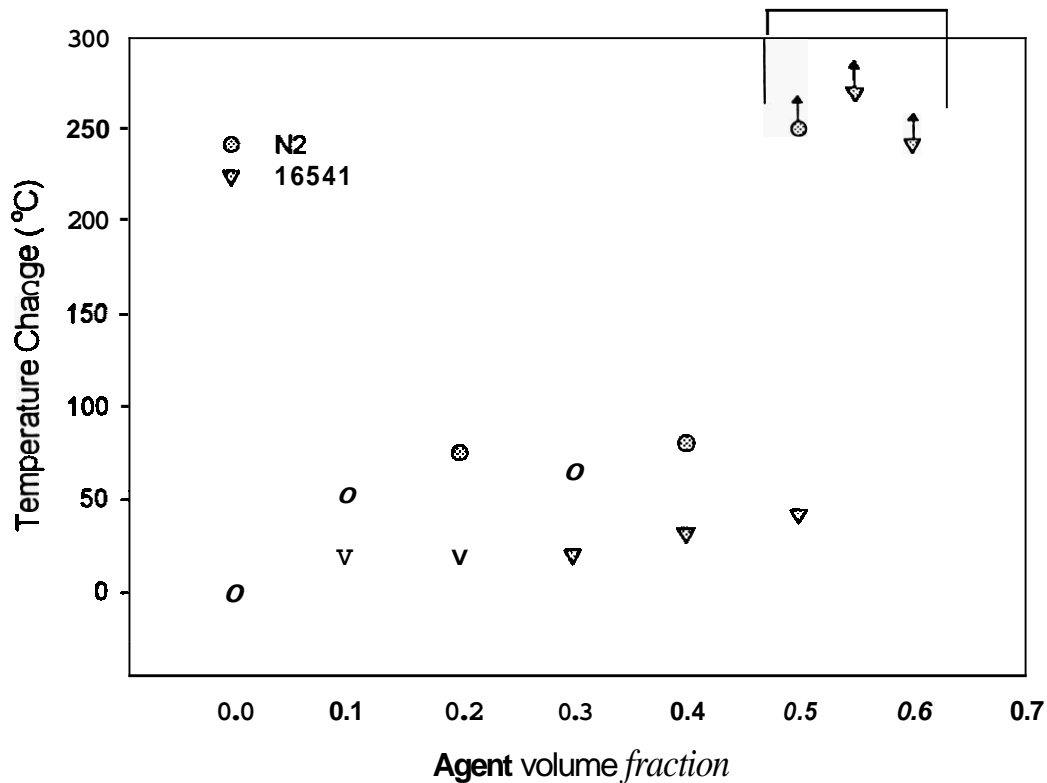
Figure 2. Change in ignition temperature **of** a stoichiometric **mixture** of ethene and air with **varying** concentrations of nitrogen, N,, and IG-541, inert gaseous agents.

flame was observed. **A** transition concentration existed for some agents where chemical reactions were observed as flashing, flickering, or glowing near or attached to the hot nickel foil. In a nonuniform mixture of agent and combustible gases, these reactions may self-propagate, resulting in reignition.

Figure 3 shows the effect of increasing HFC-23 (CHF_3) and HFC-227ea (C_3HF_7) concentration on the ignition temperature of a stoichiometric mixture of ethene-air. Comparable to the inert agents, the data indicate that increasing HFC-23 concentration resulted in an increase in the nickel metal foil temperature necessary to cause ignition of the fuel-air mixture. The temperature increased From 12°C at 0.05 to over 100°C at a 0.20 HFC-23 volume fraction. At 0.25 of HFC-23, no ignition was observed at a maximum nickel foil temperature of 220°C above the normal ignition temperature of an ethene-air mixture. This is indicated by an up-arrow attached to the

symbol. Ignition may occur at higher metal surface temperatures. Similar data for HFC-227ea show that, at agent volume fractions of less than 0.08, the ignition temperature of the ethene-air mixture is reduced. At these concentrations, the presence of the agent appears to enhance the ignition propensity of an ethene-air mixture. Except for a volume fraction of 0.122 HFC-227ea, at agent volume fractions above 0.08, increasing the concentration of HFC-227ea resulted in an increase in the ignition temperature of the mixture. Above 0.15, no ignition was observed. At 0.25 agent volume fraction, light gray smoke was visible at the top of the heated nickel foil. Hamins and Borthwick [3] noted that, while concentrations of HFC-227ea above 0.10 would not support flaming ignition in a mixture of methane-air, black smoke was observed to roll off the hot metal surface.

Figure **4** shows the effect of increasing FC-218 (C_3F_8) and FC-3-1-10 (C_4F_{10}) concentrations on the ignition temperature of a stoichiometric mixture of ethene and air. **As** in the other cases, the flame position shifted to the heated nickel surface as agent concentration was increased. For FC-218, the data show a small dependence of ignition temperature on agent volume fraction between 0.05 and 0.11. Between 0.11 and 0.20, no appreciable change in ignition temperature was noted. At 0.18 and 0.20, ignition was noted as a **series** of random intermittent flashes -- this is noted on the figure. At low volume fractions of FC-3-1-10, between 0.03 and about 0.09, the data show a small enhancement in the ignition of ethene and air mixture, i.e., reduction in the nickel foil temperature that results in ignition of the mixture. **As** the agent volume fraction is increased to 0.09, the enhancement is reduced. Above about 0.09, FC-3-1-10 suppresses the ignition of ethene-air mixture, i.e., requires higher nickel foil surface temperatures. **As** the concentration is increased, the nature of the ignition process changes. Below 0.15 there is a distinct flaming ignition event. The location of the stable flame moves from the surface of the burner to the surface of the heated nickel foil. Over the range of 0.16 to 0.19 ignition becomes difficult to define because of the intermittant flashing. The temperature over this regime is approximately 70°C above the normal ignition temperature of an ethene-air mixture. Above 0.20, foil temperature increases of about 170°C are accompanied by a glow, which may indicate combustion. Under these conditions, the ignition event is very difficult to define. It is possible that these concentrations represent a "no ignition" condition. In order to verify "no ignition" at these concentrations, additional work is necessary to determine the nature of the exhaust gases.
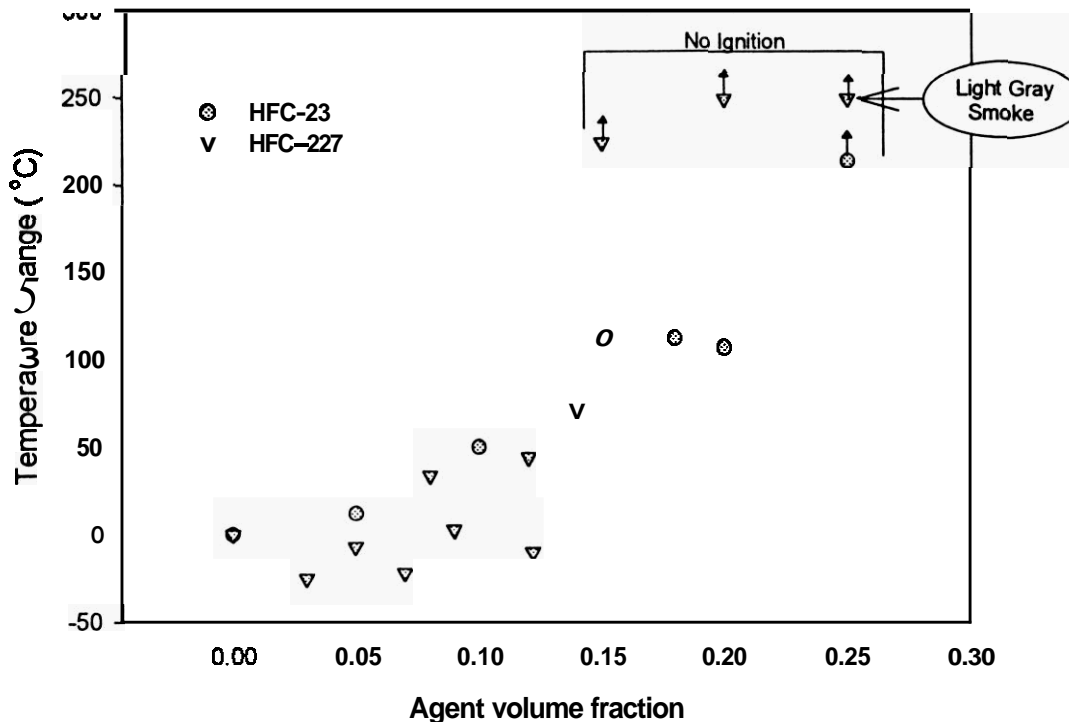
Figure 3. Change in ignition temperature of stoichiometric mixture of ethene and air as a function of *volume* fraction of HFC-23, CHF,, and HFC-227ea, C₃HF₇, gaseous agents.

At a volume fraction of about 0.28, no ignition **was** observed for FC-3-1-10

5. Discussion

The fire suppressant effectiveness of **six** clean agents was evaluated using a hot surface ignition apparatus. Agent effectiveness is defined as the volume fraction necessary to suppress ignition. The lower the volume fraction the more efficient the agent. Prior work [3] showed that in a stoichiometric ethene-air mixture the addition of halon 1301, at a volume fraction of 0.01, increased the ignition temperature of the mixture about 220°C. Only CF_3I at a volume fraction of about 0.015 was found to be nearly as effective in suppressing ignition [3]. Based on a similar testing protocol, the effectiveness of the current agents ranged from 0.20 to 0.50. Table 2 is a tabulation
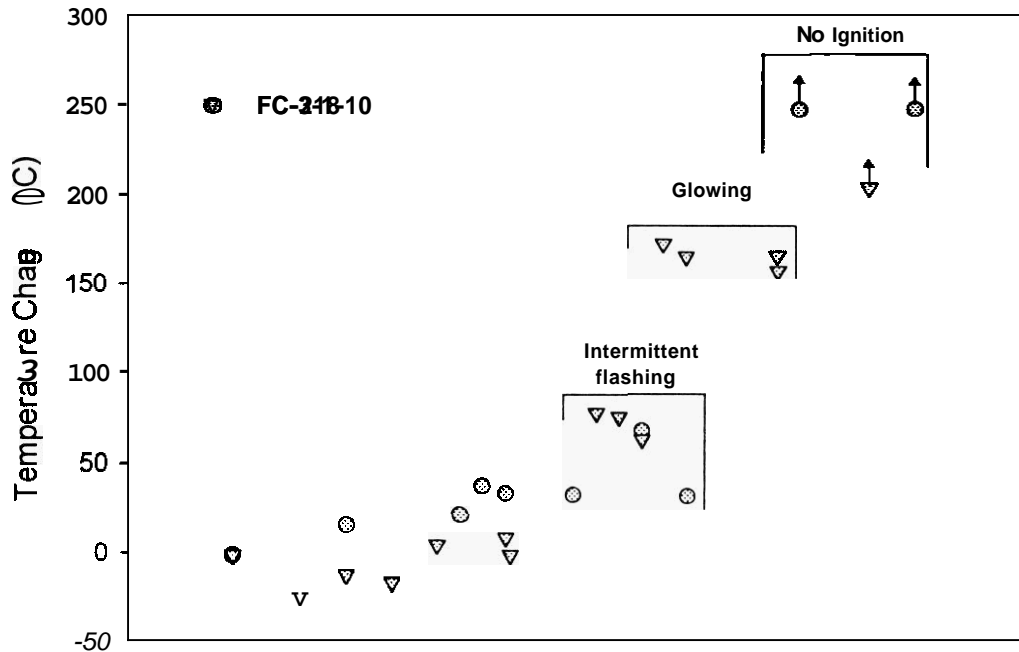
Figure **4.** Change in ignition temperature of stoichiometric mixture **of** ethene and air **as** a function **of gaseous** agent **volume** fraction for **FC-218** C_3F_8, and **FC-3-1-10** C_4F_{10}.

of published cup burner suppressant volume fraction and comparison to the results of the hot surface ignition apparatus on a volume fraction basis. The presence of a hot surface approaching 1000°C required an increase in agent concentration of 1.1 to 5.9 times that reported in cup burner tests. Previous work by **3M** [2] showed that the presence of a hot wire in the cup burner, which represents a shorter residence time in comparison to the current work, required increased suppressant concentration by a factor of 2. This **is** consistent with the work of Sano and Yamashita [5] on premixed methane air mixtures ignited by a heated plate. They found that the ignition delay initially decreased exponentially with increasing area of the hot surface. However, for a hot surface area greater than **20** mm², the ignition delay approached a constant value.

As seen in Table 2, to prevent ignition under conditions of exposure to a hot surface requires a higher volume fraction of agent than the NFPA 2001 recommended values for total flooding

applications. Table 3 presents the same results on a mass fraction basis. The data show that approximately **1.2** to **2.6** times more agent is necessary to suppress ignition in the presence of a hot surface.

Hamins and Borthwick [3] measured ignition enhancement of premixed methane-air for C_2HF_5 and C_3HF_7 up to a volume fraction of **0.15** and **0.10,** respectively. The same ignition enhancement, manifested by a lowering *of* the ignition temperature of the ethene-air mixture **as** compared to the reference case, was observed in these experiments for C_3HF_7 and C_4F_{10} for agent volume fraction below 0.08 and 0.09, respectively. While the effect is small, it is measureable. Above these values, increased agent volume fraction required higher surface temperatures to initiate ignition of the mixture.

Table 2. Comparison of published cup burner data and results of hot *surface* ignition apparatus (volume fraction)				
Agent	Cup Burner	Cup Burner (+20%)	Hot **Surface**	Ratio of **(Hot Surface)** to (Cup Burner)
N_2	0.29 - 0.35	0.35 - 0.42	0.40 - 0.50	1.1 - 1.7
IG-541	0.26 - 0.32	0.31 - 0.38	0.50 - 0.55	1.6 - 2.1
HFC-23	0.11 - 0.14	0.13 - 0.17	0.20 - 0.25	1.4 - 2.2
HFC-227ea	0.059 - 0.073	0.071 - 0.088	0.14 - 0.IS	1.9 - 2.5
FC-218	0.057 - 0.069	0.068 - 0.083	**0.20** - 0.25	3.0 - 4.4
FC-3-1-10	0.048 - 0.058	0.058 - 0.070	0.24 - 0.28	4.1 - 5.9

Agent	Cup Burner	**Hot Surface**	Ratio of (Hot **Surface) to** (Cup Burner)
N_2	0.28 - 0.35	0.39 - 0.49	1.2 - 1.8
IG-541	0.29 - 0.36	**0.54 - 0.59**	1.5 - 2.0
HFC-23	0.23 - 0.28	0.38 - 0.45	1.4 - 2.0
HFC-227ea	0.27 - 0.32	0.49 - 0.51	1.5 - 1.9
FC-218	0.29 - 0.33	0.62 - 0.68	1.9 - 2.3
FC-3-1-10	0.29 - 0.34	0.72 - 0.76	2.1 - 2.6

6. Conclusions

When exposed to a heated surface, the ignition temperature of **a** stoichiometric **mixture** of ethene-air was found to be 750 * 34°C. In general, the addition of a clean agent in the fuel-air stream requires higher foil surface temperatures than when no agent is present. However, it was found that two agents (HFC-227ea and FC-3-1-10) slightly enhanced the ignition of ethene-air, i.e., lowered the ignition temperature, at volume fractions below 0.08 and 0.09, respectively. The volume fraction of agent necessary to prevent ignition of a stoichiometric mixture of ethene and air **was** found to be 1.1 to 5.9 times greater than that found with the cup burner test apparatus.

7. References

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