EXTINGUISHMENT OF DIFFUSION FLAMES OF POLYMERIC MATERIALS BY HALON 1301

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ABSTRACT

Halon 1301 flame extinction results **are** discussed for the combustion of polymethylmethacrylate (PMMA), eight composite materials, and carbon in the gas phase. Two types of combustion and flame extinction experiments were performed: 1) in the Factory Mutual Research Corporation (FMRC) 50 kW-Scale Apparatus for PMMA and composite materials, and **2)** in the **FMRC** Elecmcal ***Arc*** Apparatus for carbon in the gas phase.

For char forming composite materials, mass transfer from the surface was low, turbulent diffusion flames were not generated, and flame extinction occurred between 3 to **4.5** % of Halon 1301, close to the value reported for the laminar diffusion flames of polymers. For noncharring PMMA, mass transfer from the surface was high, flames were turbulent, and flame extinction was found at about **6 %** of Halon 1301, contrary to the accepted value of about **4** % for the laminar diffusion flames of polymers. The conditions with Halon 1301 for flame instability and extinction for combustion efficiency less than about 0.40, with significant increase in the amounts of products of incomplete combustion, such as CO and hydrocarbon, was in agreement with flame instability and extinction found for fuel-rich conditions inside well-ventilated laminar and turbulent diffusion flames, in ceiling layers of combustion products, in enclosure fires, in ventilationcontrolled buoyant diffusion flames of polymers and for flame extinction of heptane flames by water.

Experiments in the FMRC Elecmcal Arc Apparatus showed that in the gas phase combustion, in the gas phase, in high energy arc, chemical heat release rate and combustion efficiency decreased with increase in Halon 1301. At about 7.5 % of Halon 1301, conditions were close to flame extinction and at 9.0 %, oxidative pyrolysis condition for carbon were indicated. Concentrations of Br^- and F^- ions, generated from the decomposition of Halon 1301, were also **measured.** Concentration of Br^- ion was higher than the concentration of F^- ion, although there **are** three F atoms and only one Br atom in Halon 1301. There was brown deposit on the walls of the apparatus with extensive corrosion of rubber gaskets, electrical fan, and other components.

These techniques appear to be attractive for the assessment of flame extinguishability and corrosive characteristics of fire suppressants to replace ozone layer depleting Halons.

INTRODUCTION

For the prevention of loss of life and property in fires, both active and passive fire protection techniques are used. Passive fire protection techniques deal with the prevention of fire by: 1) using materials with high resistance to ignition and fire propagation, 2) by incorporating fire retardants with the materials, 3) by coating and wrapping the surfaces, 4) by separating materials by inert fire barriers, by modifying configuration and arrangement of materials, etc. Active fire protection techniques deal with the application of flame extinction agents to fire. The most commonly used liquid and gaseous agents at the present time are water, CO_2, N_2, and Halon 1211 ($CBrClF_2$), 1301 ($CBrF_3$), and 2402 ($CBrF_2CBrF_2$). Because of the contribution of Halons to depletion of the stratospheric ozone layer, they will not be used in the future. There is thus an intense effort underway to develop alternative fire suppressants to replace ozone layer depleting Halons.

Flame extinction by liquid and gaseous agents is mainly due to physical processes (such as removal of heat from the flame and burning surface and creation of non-flammable mixture) and/or chemical processes (such as termination of chemical reactions) [1]. The effectiveness of water is mainly due to removal of heat from the burning surface as a result of vaporization. The effectiveness of Halons is mainly due to termination of chemical reactions. N_2 and CO_2 are effective mainly due to creation of non-flammable mixtures by reducing mass fraction of oxygen (Y_o).

Kodama, Miyasaka, and Fernandez-Pello [2] show that flame extinction distance over the surface of a thick sheet of a material increases with increase in gas velocity and decrease in Y_o; flame extinction is predicted to occur at $Y_o = 0.18$. Experimentally, for PMMA, flame extinction is found by Kulkami and Sibulkin [3] to occur at $Y_o = 0.181$ for 0.07 m wide, 0.19 m high, and 0.019 m thick vertical slab and by Tewarson and Ogden [4] at $Y_o = 0.178$ for 0.10 m wide, 0.025 m thick, 0.30- and 0.61-m-high vertical slabs and 0.025 m diameter, 0.61-m-high vertical cylinders. For $Y_o \leq 0.201$, flames were found to be unstable and faint blue in color [4].

Tewarson and Pion [5] find that flame extinction by reduced Y_o values depends on the fuel mass transfer (flame turbulence) for rectangular and circular horizontal PMMA slabs, 0.06 to 0.10 m^2 in area and 0.03 to 0.05 m in thickness. For sample exposed to external heat flux values of 0, 40, 60, and 65 kW/m^2, flame extinction occurred at Y_o = 0.178, 0.145, 0.134, and 0.128 respectively [5]. The Y_o value for flame extinction without external heat flux agrees with the other studies [4-7]. Thus for buoyant turbulent diffusion flames, flaming can occur up to relatively low Y_o values, the only condition is that in the gas phase the reactant-oxidizer mixture is within the flammability limit.

Tewarson [6] points out that flame instability and extinction are also found inside well-ventilated laminar and turbulent diffusion flames, in ceiling layers of combustion products, in enclosure fires and ventilation-controlled buoyant diffusion flames of polymers. At the fuel-rich boundary, flames become unstable and are extinguished for equivalence ratio greater than 2, where combustion efficiency is less than about 0.40 [6]. Equivalence ratio is the fuel-to-air mass ratio normalized by the stoichiometric fuel-to-air mass ratio. Combustion efficiency is defined as the ratio of chemical heat release rate to heat release rate for complete combustion [7]. Chemical heat is defined as the heat produced in reactions associated with the generation of CO and CO_2 and consumption of O_2 [7]. Similar results are found by Tewarson [8] for extinction of heptane flames by water, flames were unstable and were extinguished when combustion efficiency was less than or equal to 0.40.

It has been suggested by several researchers that there is a critical mass transfer from the fuel surface, at or below which ignition or combustion cannot be sustained and flame is extinguished. For example, for piloted ignition of 0.10 m diameter and 0.025 m thick horizontal granular PMMA, the critical mass transfer from the fuel surface is 0.0032 kg/m^2 s [6]. For flame extinction of 0.178 m wide, 0.356 m high, and 0.05 m thick vertical PMMA slab by water sprays, the critical mass transfer from the fuel surface is 0.0037 kg/m^2 s [9].

It thus appears that for flame extinction, it is necessary to consider differences between laminar and turbulent conditions in flames. It also appears that critical condition for flame extinction occurs when combustion efficiency is reduced below about 0.40. Ewing, Hughes and Carhart [10] have developed empirical relationship which correlates and predicts the fire suppression effectiveness of a wide variety of gases, liquid, and solid agents. Sheinson, Penner-Hahn and Indritz [11] have examined the physical and chemical action of fire suppressants to provide guidance in selecting alternative fire suppressants to replace ozone layer depleting Halons. In order to further explore these ideas, we have performed two sets of experiments in the:
1) Factory Mutual Research Corporation (FMRC) 50 kW-Scale Apparatus, shown in Fig. 1, where combustion and flame extinction experiments with Halon 1301 were performed by exposing horizontal 100 x 100 mm slabs[1] of PMMA and composite materials to an external heat

flux of 50 kW/m^2 and 2) FMRC Electrical Arc Apparatus, shown in Fig. 2, where carbon combustion in the gas phase and flame extinction experiments, using Halon 1301, were performed. In this paper, some preliminary results have been discussed.

EXPERIMENTAL APPARATUS

FMRC 50 kW-Scale Apparatus

The apparatus is shown in Fig. 1. In the experiments, 0.10 m x 0.10 m x 0.025-m-thick horizontal[2] slabs of PMMA and eight composite materials were used. The data for composite materials are taken from Ref. 12.

The apparatus consists of a lower section and an upper section. The lower section is used for the measurements of time to ignition, mass loss rate and concentrations of Y_o and gaseous agents and water application rate required for flame extinction. The upper section is used for the measurements of total mass and volumetric flow rates of combustion products-air mixture, temperature, concentrations of CO, CO_2, O_2, total gaseous hydrocarbons, H_2O, particulates, and other combustion products and optical transmission, corrosive nature of the combustion products-air mixture, and electrical charge on particulates.

Lower Section

The sample is placed on a platform connected to a load cell to measure the mass transfer of fuel vapors from the surface. In this study, experiments were performed under co-flow conditions by placing the sample inside an airtight quartz tube, 162 mm in diameter and 432 mm in length with a 260 mm long aluminum extension with an air distribution section at the bottom. Normal air with variable Halon 1301 concentration was introduced into the Apparatus. In the co-flow experiments, normal air velocity was maintained constant (0.18 m/s) for well-ventilated conditions. Several flame extinction experiments were performed with Halon 1301 at a constant external heat flux of 50 kW/m^2.

Upper Section

In this section, all the compounds generated during combustion and flame extinction are captured, along with ambient air in the sampling duct. In the duct, all the measurements are made about six diameter downstream, where temperature and concentration profiles are almost flat across the duct. The duct has been designed so that convective heat losses to the duct wall from the flowing hot chemical compounds-air mixture are negligible.

Measurements are made in the duct every 1 to 3 seconds. The generation rate of each combustion product (G_j) is calculated from the volumetric flow rate of combustion products-air mixture through the sampling duct and the concentration and density (at the gas temperature) of the products. The volumetric flow rate of air through the duct is about **20** times the rate for chemical compounds. Heat release rate is calculated from the following equations [7]:

$$\dot{Q}_{ch} = \Delta H^*_{co2} \dot{G}_{co2} + \Delta H^*_{co} \dot{G}_{co} \tag{1}$$

$$\dot{Q}_{ch} = \Delta H^*_{ox} \dot{C}_o \tag{2}$$

$$\Delta H^*_{co2} = \Delta H_T / \Psi_{co2} \tag{3}$$

$$\Delta H^*_{co} = (\Delta H_T - \Delta H_{co} \Psi_{co}) / \Psi_{co} \tag{4}$$

$$\Delta H^*_{o} = \Delta H_T / \Psi_{o} \tag{5}$$

where $\dot{Q}_{ch}$ is the chemical heat release rate (kW), $\dot{G}_{co}$ and $\dot{G}_{co2}$ are the generation rates of CO **and** CO_2 respectively (kg/s) and $\dot{C}_o$ is the consumption rate of O_2 (kg/s) ,ΔH^*_{co2} is the heat of combustion per unit mass of CO_2 generated (kJ/kg), ΔH^*_{co} is the heat of combustion per unit mass of CO generated (kJ/kg), ΔH^*_{o} is the heat of combustion per unit mass of O_2 consumed, ΔH_T is the net heat **of** complete combustion (kJ/kg), and Ψ_{co} and Ψ_{co2} are the maximum possible stoichiometric yields **of** CO and CO_2, respectively (kg/kg). For PMMA, $\Psi_{co2} =$ ***2.20*** kg/kg, $\Psi_{co} =$ 1.40 **kgkg**, Ψ_o = 1.92 kg/kg, ΔH_T = 25,200 **kJ/kg**; ΔH^*_o = 13,130 kJ/kg, ΔH^*_{co2} = 11,450 kJ/kg **and** ΔH^*_{co} = **7,870** kJ/kg. Chemical heat is released as convective and radiative heat.

The combustion efficiency, χ_{ch} ,is defined as [7]:

$$\chi_{ch} = \dot{m} \Delta H_{ch} / \dot{m} \Delta H_T \tag{6}$$

where $\dot{m}$ **is** the **mass** transfer rate from the fuel surface (kg/s), ΔH_{chem} is the chemical heat of combustion (kJ/kg).

The yield of a product, y_j, is defined as [7]:

$$y_j = \dot{G}_j / \dot{m} \tag{7}$$

where y is in kg/kg, $\dot{G}_j$ is the generation rate of product j (kg/s).

FMRC Electrical Arc Apparatus

The apparatus is shown in Fig. 2. It consists of an airtight 0.0283-m^3 square box, made from 0.013 m thick clear polycarbonate sheets with the bottom sheet was covered with a marinite sheet. The arc is generated by using two 6 mm diameter and 300 mm long copperclad carbon electrodes. The electrodes are located in the center of the box. One electrode is fixed, while the other one is connected to a linear positioning slide arc adjuster. Direct current source is used to generate continuous arcing by adjusting the gap between the electrodes. In this study, Halon 1301 was introduced into the box through an opening port and was mixed with air inside the enclosure with a fan. Concentration of Halon was measured by an analyzer. Fig. 3 shows energy in the arc as a function of time, used in this study. It can be noted that energy decreases with increase in Halon 1301 concentration. The experimental duration was about 4 minutes.

In the experiments, combustion of carbon in the gas phase in the presence of various concentrations of Halon 1301 was examined. Carbon is gasified from the electrodes due to high energy in the arc (Fig. 3). In the study, measurements were made for CO_2 concentxation generated from the combustion of gasified carbon, using a gas chromatograph, and F^- and B r ions generated from decomposition of Halon 1301, using ion-selective electrodes. Chemical heat release rate was calculated from the mass of CO_2 generated divided by the time duration of the experiment, using Eq. (1).

EXPERIMENTAL RESULTS AND DISCUSSION

PMMA in FMRC 50 kW-Scale Apparatus

Figure 4 shows plots of combustion efficiency, yield of CO (y_{co}) and yield of hydrocarbons (y_{ch}) versus Halon 1301 concentration for the flame extinction experiments for PMMA for external heat flux of 50 kW/m^2. The combustion efficiency decreases with increase in Halon concentration, and at about 5.5 %, where combustion efficiency is about 0.42, flames become unstable and are extinguished at about 6 % where combustion efficiency is below about 0.40. The data in Fig. 4 also show that decrease in combustion efficiency is accompanied by significant increase in the yields of CO and hydrocarbon, suggesting extensive chemical changes in the combustion of PMMA by Halon 1301, as expected.

The conditions with Halon 1301 for flame instability and extinction occurring when combustion efficiency is less than about 0.40 and significant increase in the amounts of products of incomplete combustion, such as CO and hydrocarbons, are in agreement with flame instability and extinction found for fuel-rich conditions inside well-ventilated laminar and turbulent diffusion flames, in ceiling layers of combustion products, in enclosure fires, in ventilation-controlled buoyant diffusion flames of polymers [6] and for flame extinction of heptane flames by water [8].

Composite Materials in FMRC 50 kW-Scale Apparatus

Figure 5 shows data for Halon 1301 concentration for flame extinction for the composite materials exposed to 50 kW/m^2 of external heat flux, where data are taken from Ref. 12. All these materials, flame extinction occurs between 3.0 to 4.5 % of Halon 1301 concentration, which is within the range of value reported for the laminar diffusion flames of polymers. In the experiments, flames did not become turbulent as the mass transfer from the surface was low due to surface charring.

Combustion of Carbon in the Gas Phase in FMRC Electrical Arc Apparatus

In the experiments, combustion of carbon in the gas phase was examined in the presence of various Halon 1301 concentrations. When the electrical arc was turned on, carbon electrodes were found to gasify and generate round reddish-white flames covering the gap between the electrcdes. The flames were due to the combustion of carbon with oxygen in the gas phase. Table 1 list the data for the chemical heat release rate at various Halon 1301 concentrations. As mass transfer from the graphite electrodes could not be measured, the combustion efficiency was not calculated directly. It was, however, assumed that for 0% Halon 1301 concentration, the combustion was complete.

Table 1

Chemical Heat Release Rate in the Combustion of **Carbon**
in the Gas Phase in Elecmcal Arc With Halon 1301

Halon 1301 (%)	Chemical Heat Release Rate (kW)	Combustion Efficiency
0.0	0.102	1.0
2.5	0.098	0.96
4.0	0.095	0.93
5.0	0.080	0.78
7.5	0.039	0.38[a]
9.0	0.012	0.12[b]

[a] Close to flame extinction, some smoke

[b] oxidative pyrolysis, no visible flame, flashing of arc.

The data in Table 1 show that chemical heat release rate and combustion efficiency decrease with increase in Halon 1301 concentration. At about 7.5 % of Halon 1301, conditions close to flame extinction are indicated and at 9.0 %, oxidative pyrolysis condition for carbon is indicated.

In the experiments, concentrations of Br^- and F^- ions, generated from the decomposition of Halon 1301, were also measured. The data are shown in Figs. 6 and 7. The concentration of Br- ion is higher than the concentration of F^- ion, although there are three F atoms and only one Br atom in Halon 1301. In the experiments, formation of Br^- and F^- ions was observed to cause a brown deposit with extensive corrosion of rubber gaskets, electrical fan, and other components was noted. In full-scale hydrocarbon pool fires, Sheinson, Musick, and Carhart [13], however, found higher amounts of F^- ion than Br^- ion. The differences are probably due to sampling techniques and efficient removal of HF by various surfaces.

SUMMARY

1. The experimental techniques developed at the Factory Mutual Research Corporation for flame extinction **of** buoyant turbulent diffusion flames and flames supported by electrical **arc,** appear to be attractive techniques to assess flame extinguishability and corrosion characteristics of alternative fire suppressants to replace ozone layer depleting Halons;

2. The criteria for flame instability and extinction under fuel-rich condition, where combustion efficiency is reduced to below 0.40 appears to be similar for various extinguishing agents;

3. Studies need to be continued to understand the effects of turbulence, fuel composition and environmental conditions on flame extinction using Halon alternatives.

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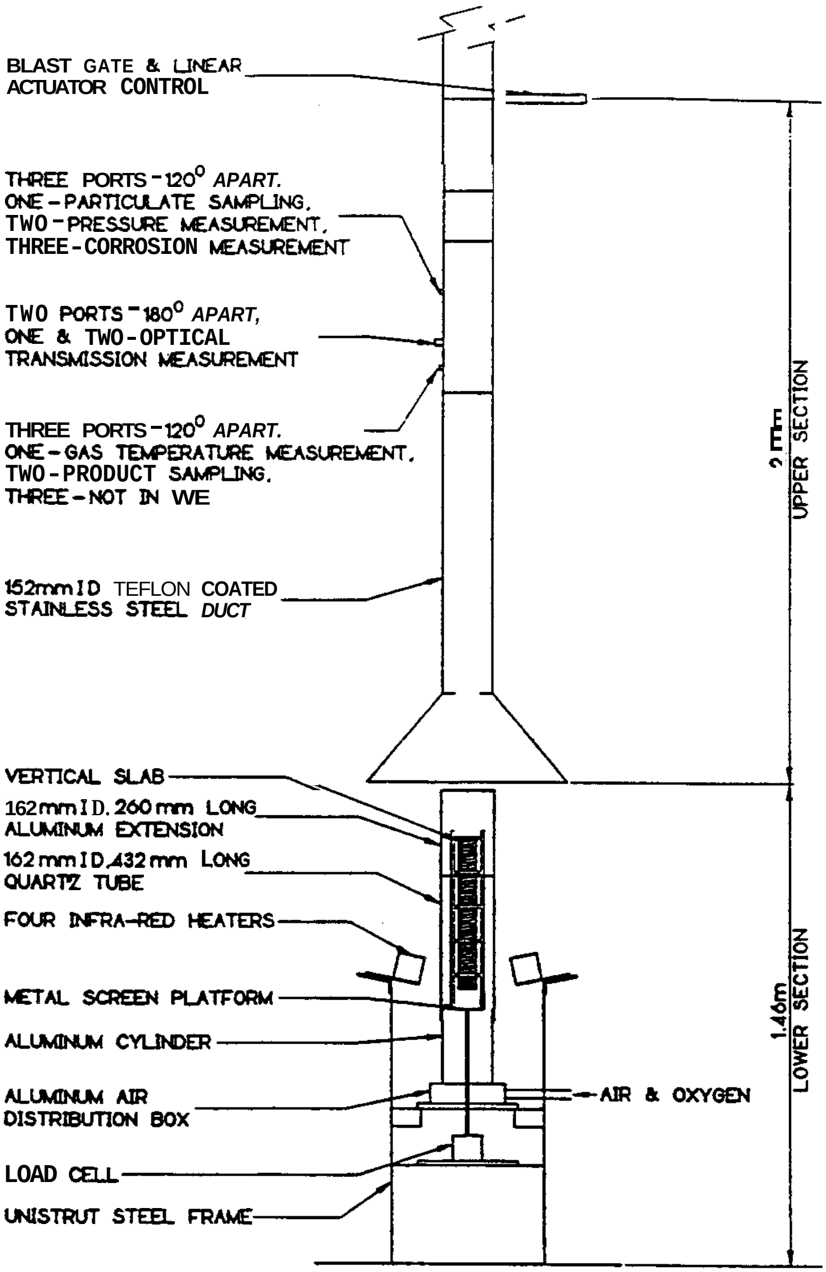

Figure 1. FMRC 50 kW–Scale Flammability Apparatus.

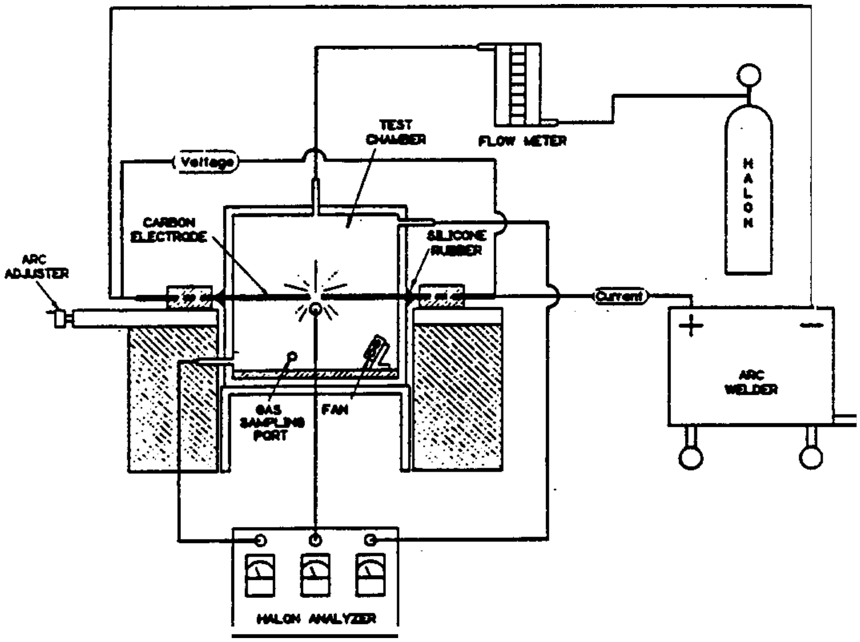

Figure 2. FMRC Electrical Arc Apparatus (not to scale).

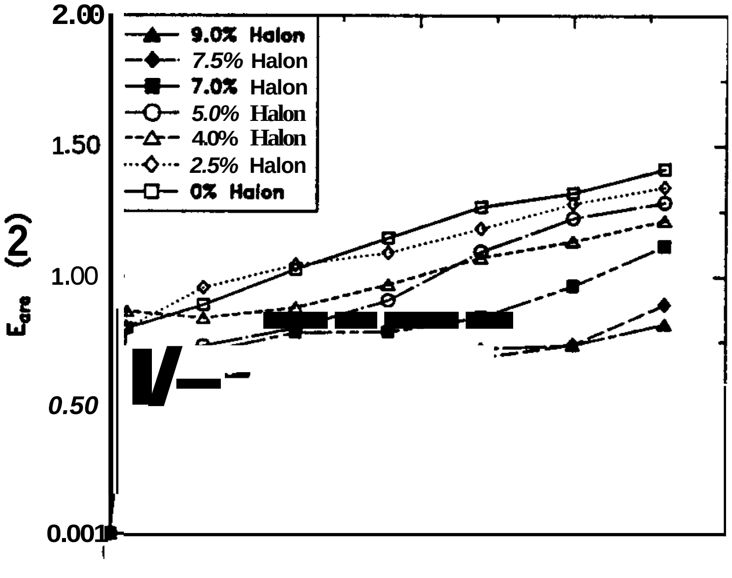

Figure 3. Arc energy at various Halon 1301 concentrations at a function of time.

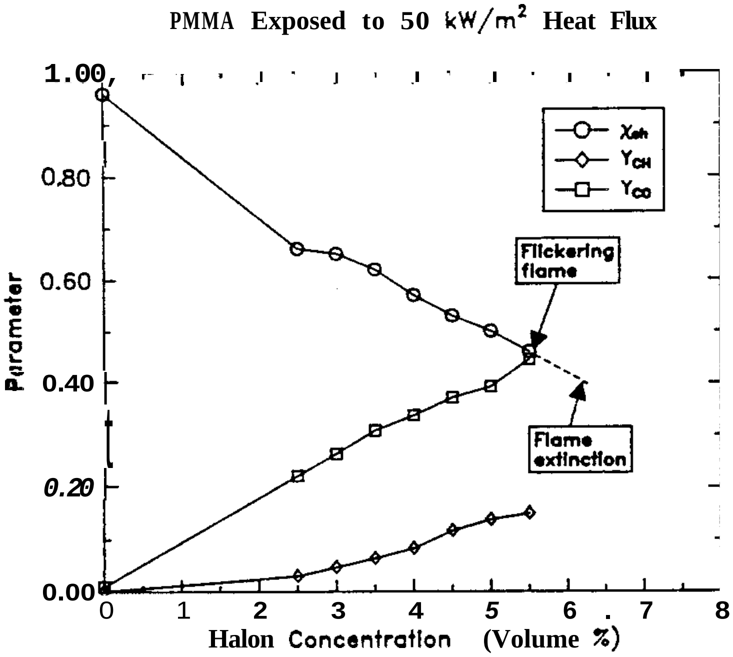

Figure 4. Combustion efficiency. yield of CO and yield of hydrocarbons of PMMA as a function of halon 1301 concentrations.

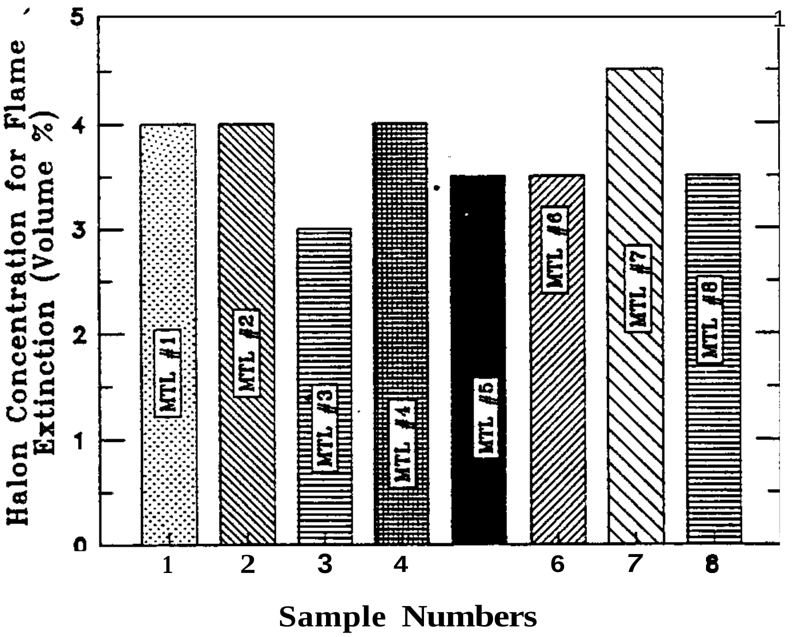

Figure 5. Halon 1301 concentrations for flame extinction for the composite polymeric materials exposed to 50 kW/m^2 external heat flux (taken from Ref.12).

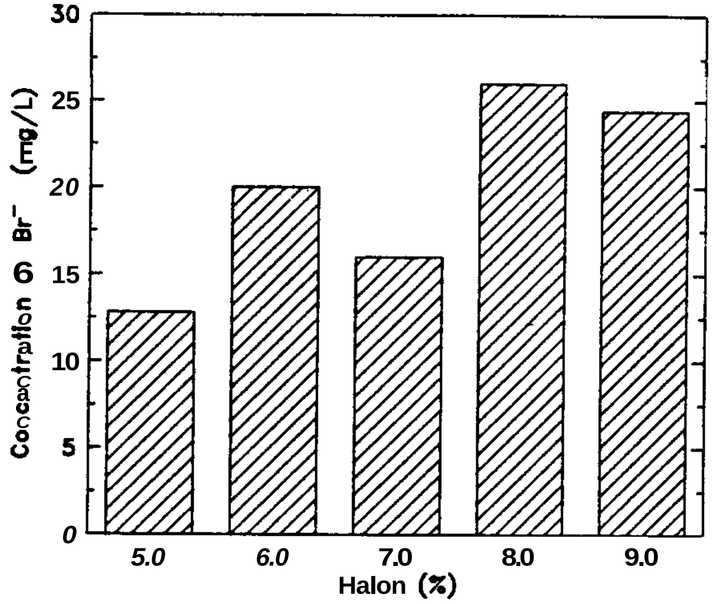

Figure 6. Concentrations of Br⁻ Ions generated from electrical arc Induced decomposition of Halon 1301.

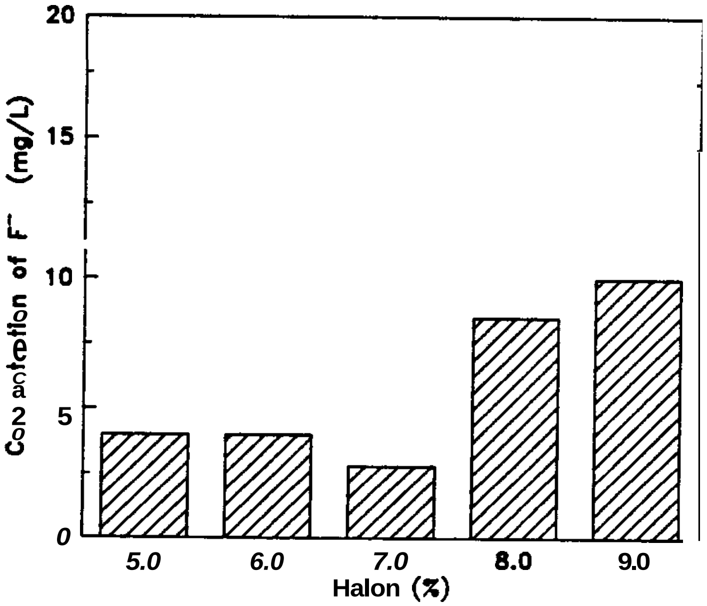

Figure 7. Concentratfons of F⁻ Ions generated from electrical arc induced decomposition of Halon 1301.