A UNIFIED MODEL OF FIRE SUPPRESSION

by

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SUMMARY

Based on the fire point equation developed by Rasbash, a unified model of fire suppression is developed. The model includes both solid and gas phase effects including surface cooling, gas phase dilution, chemical inhibition of flame reactions, and endothermic agent decomposition. The unified model is compared with available experimental data. The need for further experimental work is clearly indicated.

The model can be used to evaluate the suppressibility of various materials and as aid to agent selection for a given material. In addition, the model can be used in the development and evaluation of new suppression agents developed to replace existing environmentally objectionable agents.

INTRODUCTION

Extinguishment of solid fuel fires by water application acts primarily through the extraction of heat from the solid fuel. Evaporation of the water on the surface extracts heat, reducing the generation of fuel gases and ultimately causing extinction. Conversely, other extinguishing agents act principally in the flame to quench and retard combustion reactions. Flame extinguishing agents work by introducing additional thermal mass to the flame system and in some cases by interrupting key radical reactions in the chain reactions in the flame.

There is a need for a unified model of suppression of fire which is general enough to describe the various mechanisms of suppression used in practice. Such a unified model would be of great value in the selection of appropriate suppression agents and would be of immense value in the design of new agents to replace environmentally objectionable suppression agents.

The ignition and extinction of diffusion flames can be described by the fire point equation as developed by Rasbash[1]. This equation will first be outlined and will then be developed as a unified model which can be used to evaluate the suppressibility of materials, to select the most appropriate agent for a given material, and to guide the development of new suppression agents.

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THE FIRE POINT EQUATION

The fire point equation was first developed and described by Rasbash[1] as an engineering method for the evaluation of the conditions required for sustained piloted ignition and extinction of an existing flame. The equation is based on an energy balance at the fuel surface and a model for extinction of a gaseous flame. It is sufficiently general to include the effects of external radiation, the action of extinguishing agents, and fire retardants. In its simplest and most used form the theory is quasi-steady, but the theory can be generalized to consider transient conditions.

The burning rate of a solid fuel is described by an energy balance at the fuel surface, which can be written as

$$\dot{m}'' = \frac{f \Delta H_c \dot{m}'' + \dot{Q}_E'' - \dot{Q}_L''}{L_V} \qquad (1)$$

where $\dot{m}''$ is the burning rate per unit area, f is the fraction of heat released which is transferred back to the fuel surface, ΔH_c is the heat of combustion of the fuel volatiles, $\dot{Q}_E''$ is the externally applied heat flux, $\dot{Q}_L''$ is the heat lost from the surface, and L_v is the heat of gasification. In the most general case, f includes both radiative and convective heat transfer to the surface, $\dot{Q}_L''$ includes losses both through the solid and by reradiation from the surface, and L_v may vary with time.

The extinction condition is defined by the conditions under which the gaseous flame above the surface can no longer be sustained. The quenching of a diffusion flame can be described in terms of the fraction of heat generated which must be lost to cause the flame to be quenched, ϕ. It is known that for both premixed and diffusion flames there exists a critical adiabatic flame temperature for limit flames[2]. If the adiabatic flame temperature is reduced below the critical temperature (1700 K for most fuels), the flame will extinguish. Similarly, if the flame is placed in an environment in which heat is lost to adjacent surfaces, the flame will be extinguished if these losses cause the flame temperature to be sufficiently reduced. The value of ϕ is in the range 0.1 to 0.4[1,3] in ambient air depending on the reactivity of the fuel gases. Rasbash argues that ϕ is a parameter describing the influence of chemical kinetics. The introduction of gas phase fire retardants and chemically active extinguishing agents would reduce the value of ϕ. This is similar to the observation that the critical adiabatic flame temperature at the lower flammable limit is increased by the addition of halogens or other gas phase fire retardant. The range of ϕ reported may also reflect reductions in the actual heat of combustion of the volatiles relative to the theoretical heat of combustion of the original fuel. Ewing et al.[9,11,18] have developed alternate theories based on physical rather than chemical action of extinguishing agents. Either view is compatible with the methods developed in this paper.

At extinction the heat loss from the flame will be the critical fraction of the total heat released, ϕ. In this instance, the heat loss is to the fuel surface. As extinction is approached, the flames will become smaller and less luminous. As such radiation from the flame to the surface at extinction will be negligible. Under these conditions, flame heat losses are dominated by convection to the fuel surface, and the energy balance at the fuel surface at extinction becomes

$$\left(\phi \Delta H_c - L_V\right)\dot{m}_{cr}'' + \dot{Q}_E'' - \dot{Q}_L'' = 0 \qquad (2)$$

The critical mass flux at extinction, $\dot{m}_{cr}''$, is determined by the convective heat feedback process. Following Spalding's B number theory, the mass burning rate at the extinction condition is given

by

$$\dot{m}_{cr}''\dot{m}_{cr}'' = \frac{h}{c_p} \ln\left(1 + B_{cr}\right) \qquad (3)$$

where h is the convection heat transfer coefficient and B_{cr} is given by

$$B_{cr} = \frac{Y_{O2}\,\Delta H_R(O_2)}{\phi \Delta H_c} \qquad (4)$$

where Y_{O2} is the oxygen mass fraction and $\Delta H_R(O_2) \cong 13$ kJ/g for organic fuels.

For the purposes of considering extinction by water application, it is useful to separate the heat losses due to reradiation from those due to the evaporation of water. As such the normal heat losses will be included in $\dot{Q}_L''$, and losses due to water evaporation will be $\dot{Q}_W''$. Equation 2 can be rewritten as

$$\left(\phi \Delta H_c - L_V\right)\frac{h}{c_p}\ln\left(1 + \frac{Y_{O2}\Delta H_R(O_2)}{\phi \Delta H_c}\right)$$
$$+ \dot{Q}_E'' - \dot{Q}_L'' - \dot{Q}_W'' = 0 \qquad (5)$$

While Equation 5 appears to be quite complex, most of the terms are material fire properties or may be taken as a constant for a particular fuel surface orientation. For a particular material and fuel surface configuration ΔH_c, L_v, h, c_p, and $\Delta H_R(O_2)$ may be taken as constants.

APPLICATION OF FIRE POINT EQUATION TO ESTABLISH THE SUPRESSIBILITY OF MATERIALS

Water-based Extinguishing Methods

In order to evaluate the suppressibility of a material by water, it is necessary to determine the water application rate required under well specified conditions relevant to the end use of the material. A series of experiments can be conducted in which a sample is subjected to a range of constant radiant heat fluxes, and once burning the sample is subjected to a known application rate of water. At each radiant flux a range of water application rates is used to establish the minimum water application rate required for extinction, $\dot{m}_{w,cr}''$.

Having run extinguishability experiments at several incident heat fluxes, the data can be

plotted as $\dot{Q}_E''$ as a function of $\dot{m}''_{w;cr}$. The efficiency of the water applied, c_w, will depend on the ability of the spray to penetrate to the fuel surface and is expected to be approximately constant for an given experimental configuration. The heat lost in evaporating the water, $\dot{Q}_W''$, is given by

$$\dot{Q}_W'' = c_w \, \dot{m}''_{w;cr} \, L_{v;w} \tag{7}$$

where $L_{v;w}$ is the heat of gasification of water. According to Equations 5 and 7 the plot of the data, $\dot{Q}_E''$ vs $\dot{m}''_{w;cr}$, should be a straight line with a slope , $c_w \, L_{v;w}$, and an intercept, C, given by

$$C = \frac{(\phi\Delta H_c - L_v)\frac{h}{c_p} \ln\left(1 + \frac{Y_{o2}\Delta H_R(O_2)}{\phi\Delta H_c}\right) - \dot{Q}_L''}{c_w \, L_{v;w}} \tag{8}$$

Such a plot is shown in Figure 1. The value of C can be used as a figure of merit for suppressibility of the material and can be compared to other materials which are known to have acceptable suppressibility characteristics.

Magee and Reitz[4] have measured the critical water application rate as a function of the applied external radiant flux for four thermoplastic materials. Their results do in fact fall on
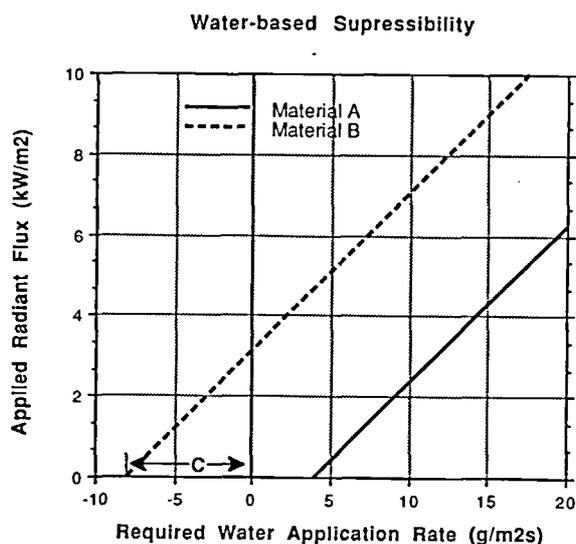
Water-based Supressibility

Figure 1. The effect of material properties and externally applied radiant flux on the water application rate required for suppression. Material A is characteristic of thermoplastic materials. Material B is characteristic of materials which will not continue burning in the absence of external radiation. Material B is more typical of the desired performance of materials.

a straight line, as Equations 5,7, and 8 predict. For vertical surfaces the slope of the line indicates an application efficiency of approximately 1.0. For horizontal samples the indicated application efficiency is approximately 1.6. This physically unrealizable application efficiency may be associated with fluid mechanical effects of a crosswind configuration, i.e., the extinction was in part aided by blow-off effects which are unlikely to contribute to extinction in real cases. Within the accuracy of the data, the slopes did not change with the material tested. Magee and Reitz found the required applied density for their four plastics to follow the trend polyethylene > polystyrene > polyoxymethylene > polymethylmethacrylate (PMMA). C could be found by independently measuring each of the thermochemical properties included in Equation 8. Using available data from Tewarson[3] yields values which are in rough agreement with Magee and Reitz's results. However, the measurement of the individual quantities is far more difficult, and the result is less reliable.

The intercept, C, is simply the water application rate required to extinguish the flame in the absence of external radiation. Figure 1 shows the behavior of two materials, A and B. Material A is characteristic of common thermoplastics materials. The intercept, C, is positive indicating that the material will burn without external radiation, and a finite application rate of water is required to extinguish the flame. As material B shows, it is possible for C to be negative, indicating that the material cannot burn without the support of radiation. Of course, the negative value of C has no direct physical meaning.

The minimum radiative flux which will sustain burning, $\dot{Q}_{EO}''$, is given by $-C \, c_w \, L_{v;w}$. While this is a positive number with direct physical meaning for materials characterized by material B, it is negative and hence nonphysical for materials characterized by material A. Since neither C nor $\dot{Q}_{EO}''$ has direct physical meaning over the full range of possible behavior, it seems preferable to simply use the intercept, C, as a means for ranking and comparing materials. The more negative C is, the better the material is from a suppressibility standpoint.

It should be noted that the slope of the curve, c_w $L_{v,w}$, is not material dependent. If c_w is known for a particular experimental configuration, then in principle experiments need only be done at one external radiant flux level. However, the radiant flux level used should be near the minimum at which burning can be achieved so that the extrapolation to zero incident heat flux is minimized. As Equation 5 suggests, it is not desirable to run extinguishability experiments at excessively high incident radiant heat fluxes since for these high fluxes the material dependent term becomes small compared to the externally applied flux. For very high heat fluxes Equation 5 could be approximated as $\dot{Q}_E'' - \dot{Q}_w'' = 0$. Clearly in this limit all materials are equally suppressible. The major task is absorbing the external radiation, not heat feedback, from the flame itself.

Flame Extinguishing Agents

Because these agents act in the flame, the response to agent application is very different than that observed for water application. First, the concentration of the extinguishing agent is the measure of the agent's application rather than the mass application rate per unit fuel surface area as was used for water. Second, the required concentration as a function of the externally applied radiation is entirely different than that shown in Figure 1 for water. Despite the major differences between water-based and flame extinguishing agents, both can be understood in the context of the fire point equation, working from Equation 5.

Since flame extinguishing agents act thermally and chemically to extinguish the flame above a material, the effects of these agents must be included in the determination of ϕ, the critical fraction of the energy release which needs to be lost to cause extinction. For water-based suppression, ϕ was simply a constant of the material, since the water has little effect on the gas phase combustion process. Of course, water sprays can act to cause flame extinguishment, but for solid fuels the fuel surface effects dominate. In the extinguishment of gaseous and liquid hydrocarbon fires, water extinguishment is via thermal effects in the flame and extinguishment should be analyzed by the methods discussed in this section.

ϕ can be modeled by making use of an analogy between limit premixed flames and limit diffusion flames. The basis of the analogy is summarized in Beyler[2]. It has been found that the adiabatic flame temperature (AFT) at the stoichiometric limit (SL) and the adiabatic flame temperature for limit diffusion flames calculated on the basis of stoichiometric mixing and combustion of the fuel and oxidant streams are equal for a given fuel. For most fuels the AFT is about 1700 K. More reactive fuels like hydrogen have lower adiabatic flame temperatures at the stoichiometric limit, $T_{AFT}(SL)$, and less reactive or retarded materials have higher values of $T_{AFT}(SL)$.

The fraction of the enthalpy of reaction that can be lost before extinction occurs at the stoichiometric limit is denoted as ϕ_{SL}, in analogy to ϕ in diffusion flames. The quantity $1 - \phi_{SL}$ is the ratio of the enthalpy in the products at the SL to the enthalpy of the products of stoichiometric burning involving normal air.

$$1 - \phi_{SL} = \frac{c_p \left(T_{AFT}(SL) - T_o \right)}{\Delta H_R(O_2) \, Y_{O_2; \infty}/(1 + r)} \tag{9}$$

where c_p is the specific heat of the products of combustion, T_o is the initial temperature of the reactants prior to combustion, $\Delta H_R(O_2)$ is the heat of reaction of oxygen, $Y_{O_2; \infty}$ is the ambient oxygen mass fraction, and r is the mass based stoichiometric fuel to air ratio. In Equation 9 the numerator is the energy contained in the products of combustion and the denominator is the energy released by stoichiometric burning of the fuel in ambient air.

Equation 9 may be generalized to nonstandard atmospheres by denoting the nonstandard ambient oxygen mass fraction as $Y_{O_2; \infty}$ and defining $r = (F/O)_{stoich} Y_{O_2; \infty}$, where $(F/O)_{stoich}$ is the mass based stoichiometric fuel/oxygen ratio $((F/O)_{stoich} = \Delta H_R(O_2)/\Delta H_C)$. The diluent effect of adding extinguishing agent on the oxygen mass fraction is given by replacing $Y_{O_2; \infty}$ with $Y_{O_2; \infty}(1 - Y_{ext})$. The introduction of the extinguishing agent also affects the heat capacity of the products of combustion. This effect may be included approximately by substituting $c_{p,o} + Y_{ext} \Delta_{cp}$ for c_p, where Δc_p is the the heat capacity of the extinguishing agent minus

the heat capacity of the products of combustion.

By the analogy between limit premixed and diffusion flames we expect $\phi=\phi_{SL}$ at extinction. Rasbash[1] has found that $\phi=\kappa \phi_{SL}$, where $\kappa=0.6$. However, this may result from errors in the deduction of ϕ in diffusion flame experiments where the flame did not cover the full fuel surface (see Roberts and Quince[5]). Given the uncertainty, we will incorporate κ into the analysis. Including κ and the generalization above, the analogy between premixed and diffusion flames yields the following from Equation 9.

$$\phi=\kappa\left(1-\frac{c_P\left(T_{AFT}(SL)-T_o\right)\left(1+r\right)+Y_{ext}\Delta c_P\left(T_{AFT}(SL)-T_o\right)}{\Delta H_R(O_2)\,Y_{O2;\infty}\left(1-Y_{ext}\right)}\right) \quad (10)$$

We will take ϕ for $Y_{ext}=0$ as ϕ_o. Using Equation 10

$$\phi_o = \kappa\left(1-\frac{c_P\left(T_{AFT}(SL)-T_o\right)\left(1+r\right)}{\Delta H_R(O_2)\,Y_{O2;\infty}}\right) \quad (11)$$

and rewriting Equation 10 in terms of ϕ_o yields

$$\phi = \frac{\phi_o - \kappa Y_{ext}\left(1+\dfrac{\Delta c_P\left(T_{AFT}(SL)-T_o\right)}{\Delta H_R(O_2)\,Y_{O2;\infty}}\right)}{1-Y_{ext}} \quad (12)$$

As expected the addition of an extinguishing agent has the effect of reducing ϕ from the normal value of ϕ_o.

Equation 12 includes within it the three mechanisms by which a flame extinguishing agent may act: dilution, added thermal capacity, and chemical inhibition. Added thermal capacity is reflected in the Δc_p term. Dilution effects are included in the $-\kappa \, Y_{ext}$ term, and chemical inhibition effects are included through increases in $T_{AFT}(SL)$.

a). Heat Capacity and Dilution Effects

Equation 12 can be used in conjunction with Equation 5 to describe the conditions under which flame extinction is expected due to gases like N_2 and CO_2 which act through heat capacity and dilution effects. Of particular interest is the relationship between the mass fraction of extinguishing agent, Y_{ext}, the externally applied radiant flux, $\dot{Q}_E''$, and the suppressibility of the fuel. Figure 2 shows a map of suppressibility in the Y_{α}'' vs $\dot{Q}_E''$ plane for PMMA with nitrogen as

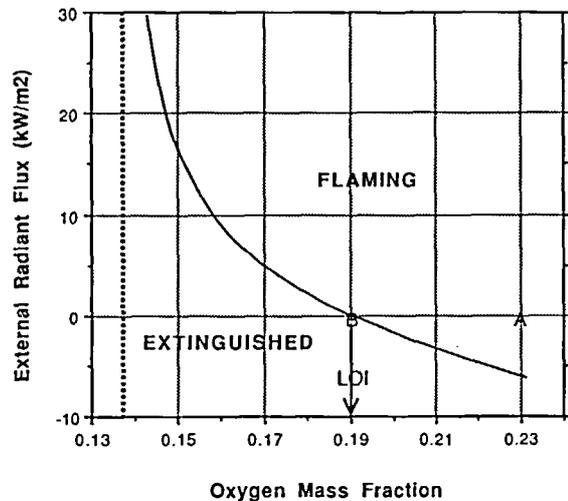**PMMA EXTINCTION BY NITROGEN**

Figure 2. Calculated Extinguishment of PMMA by Nitrogen. The mass fraction of oxygen is reduced by the addition of nitrogen to the oxidant stream. Since the heat capacity of nitrogen and oxygen are nearly equal and nitrogen is inert, extinguishment by nitrogen is purely by dilution. The predicted limiting oxygen index (LOI) is in excellent agreement with the measurements of Tewarson[3] and Fenimore and Martin[6].

the extinguishing agent developed using Equation 12.

The figure clearly shows that PMMA will burn in normal air without external radiation (see point A). As nitrogen is added and the oxygen mass fraction is reduced, the flame is extinguished at point B. The oxygen concentration at this point is known as the limiting oxygen index (LOI). The prediction of the LOI shown in Figure 2 is in excellent agreement with the measurements of Tewarson[3] and Fenimore and Martin[6].

In order to sustain a flame at oxygen concentrations below the LOI, it is necessary to provide external radiation. As the oxygen mass fraction is reduced, the required radiant flux increases and approaches infinity as $Y_{O2} \longrightarrow 0.138$. At oxygen mass fractions less than 0.138, no flame can be sustained no matter how high the incident radiant flux. At this point the extinguishment process is completely decoupled from the volatilization process. No matter what the volatilization rate, the flame will be extinguished. This is consistent with the experimental observations of Simmons and Wolfhard[7]. They studied the limiting oxygen index of gaseous fuels and observed such an extinction limit.

Figure 3 shows the mass flux of volatiles at the extinction limit as calculated from Equation 3 as well as the extinction curve from Figure 2. The figure shows the behavior of the volatilization rate as a function of the mass fraction of oxygen at extinction. As previously described, the volatilization rate increases asymptomatically as the oxygen mass fraction approaches 0.138. The volatilization rate is, however, remarkably constant well away from this limit. This predicted behavior is consistent with the measurements of Tewarson[3]. Tewarson measured the critical mass flux for piloted ignition in ambient air as 4.4 g/m^2s. Piloted ignition may be viewed as a "not extinction" point inasmuch as a pilot ignites the vapors above the material and piloted ignition is said to have occurred if the flame continues after the pilot is removed. Tewarson also measured the critical mass flux at extinction at the LOI as 4.6 g/m^2s. These values are quite close and are in good agreement with the predictions shown in Figure 3.

While extinguishment data for PMMA by carbon dioxide does not appear to be available in the literature, the expected performance can be calculated using Equation 12. In fact, on a mass basis the heat capacity of carbon dioxide is very near that of nitrogen so that they are approximately equally effective on a mass basis. This is consistent with the experimental results of Kent and Williams[8]. Figure 4 shows the carbon dioxide

mass fraction in the air stream required for extinguishment of PMMA exposed to a range of externally applied radiant fluxes. The required mass fraction of carbon dioxide more than doubles from no external flux to the gas phase limit shown by the vertical asymptote.

b). Dry Chemical and Halon Extinguishing Agents

Equation 12 can be used directly to describe the action of agents that act solely through heat capacity and dilution. It is known, however, that other processes such as kinetic chain breaking and endothermic dissociation can also act to cause extinction. Energies of dissociation of extinguishing agents act thermally in much the same way as an increased heat capacity. Including the heat of dissociation, ΔH_A, in Equation 9 yields

$$1 - \phi_{SL} = \frac{c_p\left(T_{AFT}(SL) - T_o\right) + Y_{ext}\,\Delta H_D/(1 + r)}{\Delta H_R(O_2)\,Y_{O2,\infty}/(1 + r)} \qquad (13)$$

Including dissociation has no effect on Equation 11

$$\phi_o = \kappa\left(1 - \frac{c_p\left(T_{AFT}(SL) - T_o\right)(1 + r)}{\Delta H_R(O_2)\,Y_{O2,\infty}}\right) \qquad (11)$$
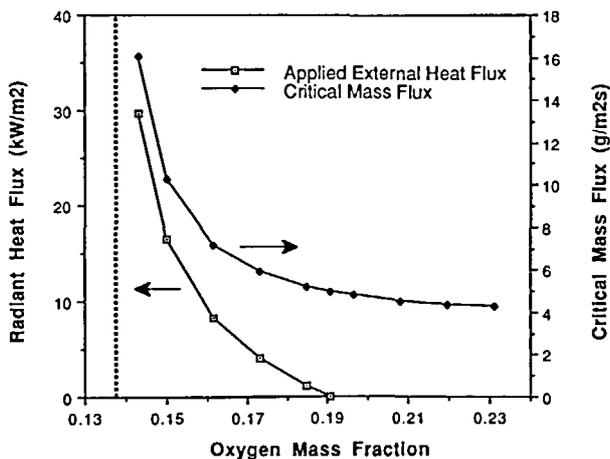
Figure 3. Critical Mass Flux at Extinction. The calculated mass volatilization rate per unit area at extinction approaches infinity as the oxygen mass fraction approaches 0.138. Away from this limit the critical mass flux is quite constant and in agreement with the measurements of Tewarson[3].
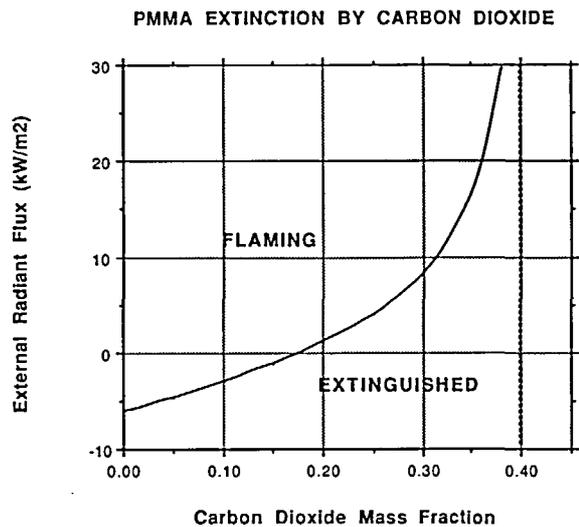
Figure 4. Calculated Extinguishment of PMMA by Carbon Dioxide. The mass fraction of carbon dioxide in the air stream required for extinguishment more than doubles from no external flux to the gas phase limit shown by the vertical asymptote.

and Equation 12 becomes

$$\phi = \frac{\phi_o - \kappa Y_{ext}\left(1 + \dfrac{\Delta c_p \left(T_{AFT}(SL) - T_o\right) + \Delta H_D}{\Delta H_R(O_2) Y_{O2;\infty}}\right)}{1 - Y_{ext}} \qquad (14)$$

Ewing, Hughes, and Carhart[9] have shown that the extinction of gaseous and liquid fuels in air by dry chemical agents can be predicted using $T_{AFT}(SL)$ = 2165 K if the agent's heat capacity and heat of dissociation are included. They further found that the performance of bromine containing halons can be predicted using $T_{AFT}(SL)$ = 2015 K and the agent's heat capacity. For chlorinated halons, they found that it was necessary to assume that due to the larger carbon-chlorine bond energy, only 30% of the C-Cl bonds are broken. Ewing et.al.[9] showed excellent agreement between theory and experiment for a wide range of dry chemical agents and halons. Their work focused entirely on gas phase effects, and did not include the condensed phase effects modeled here using the fire point equation. Fortunately, all the fuels considered by Ewing et.al.[9] were gaseous or highly volatile liquid fuels for which gas phase effects dominate. This is illustrated for heptane in Figure 5. The LOI of heptane is seen to be very near the

HEPTANE EXTINCTION BY NITROGEN

Figure 5. Extinction of Heptane by Nitrogen. Note that the limiting oxygen index (LOI) is very near the limit dictated by considering flame effects alone. This justifies the flame approach taken by Ewing et.al.[9] in considering extinguishment of gases and volatile liquids. Fuel surface effects will need to be considered for solid materials.

limit under conditions of large radiant heating where condensed phase effects can be ignored.

Unfortunately, Ewing et.al.[9] did not consider the effect of varying oxygen concentration on $T_{AFT}(SL)$ and the extent of agent dissociation. Tucker, Drysdale, and Rasbash[10] have studied the effect of oxygen concentration on the concentration of He, CO_2, and Halon 1301 required for extinguishment of heptane flames. They cast their results in terms of the % free oxygen, the oxygen concentration in excess of the LOI value. As expected, their results indicate that the required concentration of He and CO_2 increases linearly with the % free oxygen. This is consistent with the theory developed here. However, for Halon 1301 the plot of agent required versus % free oxygen was nonlinear up to 20% free oxygen (actual concentration ~ 35% by volume). At higher concentrations of oxygen the curve is linear. The curvature of the halon plot implies that the $T_{AFT}(SL)$ or the degree of dissociation are varying with the halon concentration required for extinction.

The slope of the halon/free oxygen curve in the linear region is directly related to the heat extraction efficiency of Halon 1301. The slope observed by Tucker et.al.[10] is consistent with a heat of dissociation about 30% of the value used by Ewing et.al.[9] (20 kcal/mol vs 69 kcal/mol). This is consistent with observations made by Kent and Williams[8] that much of the endothermicity of halon dissociation is lost when further reaction of the resulting Br atom is considered. It is possible that in the work of Ewing et.al.[9] a lower heat of dissociation and a higher $T_{AFT}(SL)$ might have fit the data equally well. Figure 6 shows the change in the $T_{AFT}(SL)$ with halon concentration at extinction calculated from the data of Tucker et.al.[10] using a heat of dissociation of 20 kcal/mol. The increase in $T_{AFT}(SL)$ can be interpreted as resulting from flame reaction inhibition due to kinetic effects. The efficiency of halon increases markedly with concentration up to a mass fraction of 0.2, with no further increases above this concentration. This discussion clearly indicates that extinguishment by dry chemical agents and halon are not yet well understood. Further experimental and theoretical work is required to
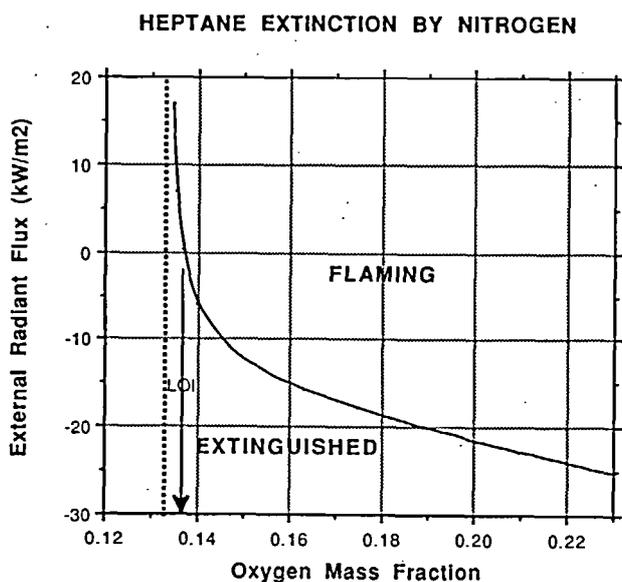
address nonstandard oxygen concentrations.

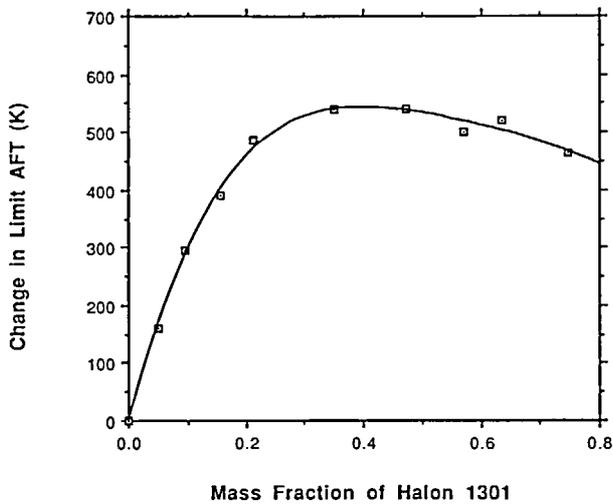**Mass Fraction of Halon 1301**

Figure 6. Calculated limit adiabatic flame temperature for the hexane extinction experiments of Tucker et.al.[10] The plot can be interpreted as evidence that the effect of halon on flame kinetics increases up to a halon mass fraction in the oxidant stream of 20% and that the kinetic effectiveness does not increase at higher concentrations.

Figure 6 suggests that for halon concentrations required for extinction of flames in normal air that the limit adiabatic flame temperature is approximately linear in the mass fraction of halon, i.e.

$$T_{AFT}(SL) = T_{AFT}(SL)_0 + k\ Y_{ext} \qquad (15)$$

Data for Halon 1301 extinction by Ewing et.al.[9] and others suggest that k = 2060 K and $T_{AFT}(SL)_o$ = 1700 K as used previously. Using these values and heat capacity and heat of dissociation from Ewing et.al.[9] yields the curve shown in Figure 7. This figure represents a preliminary calculation, but is instructive in that the general shape of the curve is not changed by the dissociation and kinetic properties of Halon 1301. It must be emphasized that additional experimental work is required for modeling the effectiveness of Halon 1301.

A similar preliminary calculation can be made for dry chemical agents. Figure 8 shows the results of such a calculation for potassium bicarbonate. Data for $KHCO_3$ extinction by Ewing et.al.[9,11] suggest that k = 14,500 K and $T_{AFT}(SL)_o$ = 1700 K as used previously. Using these values and heat capacity and heat of dissociation from Ewing et.al.[9] yields the curve

PMMA EXTINCTION BY HALON 1301
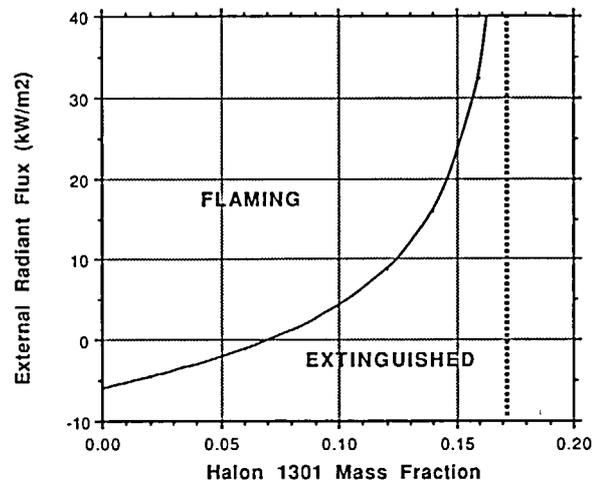

Halon 1301 Mass Fraction

Figure 7. Preliminary Calculation of PMMA Extinction by Halon 1301. This preliminary calculation assumes that $T_{AFT}(SL)$ is a linear function of the 1301 mass fraction as motivated by Figure 6. Thermophysical data taken from Tewarson[3] and Ewing et.al.[9] Note that the assumed dissociation and kinetic properties of Halon 1301 do not markedly change the shape of the curve.

shown in Figure 8. Once again, the characteristic shape of the curve is maintained. It must be emphasized that these are preliminary hypothetical calculations.

PMMA EXTINCTION BY KHCO3
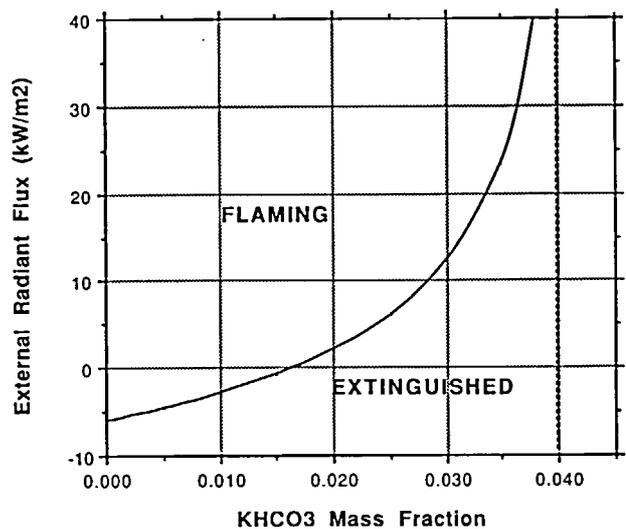

KHCO3 Mass Fraction

Figure 8. Preliminary Calculation of PMMA Extinction by $KHCO_3$. This preliminary calculation assumes that $T_{AFT}(SL)$ is a linear function of the $KHCO_3$ mass fraction as motivated by Figure 6. Thermophysical data are taken from References 3,9, and 11. Note that the assumed dissociation and kinetic properties of $KHCO_3$ do not markedly change the shape of the curve.

TESTING PROCEDURES AND DATA INTERPRETATION

The apparatus required for the study of suppressibility must be capable of evaluating a wide range of materials and all available extinguishing agents. The results need to be presented in a form in which the fire point equation and the models developed here can be applied to interpret the results. This section will discuss the requirements for the testing apparatus, procedures, and interpretation for both fuel surface and flame extinguishing agents.

The general features of the apparatus required include the ability to expose the sample to an external radiative heat flux and the ability to expose the sample to artificial atmospheres. The ability to expose the sample to an external radiant flux is included in a number of small-scale rate of heat release calorimeters, including the FMRC Flammability Apparatus[12] and the Cone Calorimeter[13]. The FMRC apparatus is normally operated with a vertical quartz tube surrounding the sample, which allows artificial environments to be used. The Cone Calorimeter does not at this time include the ability to control the composition of the air stream. However, it would in principle be possible to enclose the apparatus to allow for the use of artificial environments.

Both test methods allow the measurement of mass loss rate, heat release rate, and the generation rate of products of combustion. The FMRC apparatus uses a horizontal sample (~0.1 m), while the Cone Calorimeter can accommodate either a vertical or horizontal sample (~ 0.1 m). While in evaluating the flammability of a material, it is necessary to evaluate dripping and flowing tendencies, for the evaluation of suppressibility the horizontal orientation is probably preferred.

Neither test method includes any specific mechanism to provide forced ignition of the sample at radiant fluxes below the flux required for piloted ignition. Development of reproducible methods based on supplemental radiative heaters or flame impingement will need to be developed.

In order to determine the required water application rate or agent concentration, it is important that the extinguishment be attempted when the maximum burning rate is achieved by the sample. This presents no difficulties for simple thermoplastics with a significant steady burning period. For many materials, there will be a peak heat release rate shortly after ignition. In order to detect the maximum burning rate, it is necessary to locate a thermocouple directly above the flame. When the thermocouple output peaks, agent application should be initiated.

Water-based Agents

While much of the small-scale water-based extinguishing experiments have used spray nozzles[4,14], we have seen in the analysis of the results of Magee and Reitz[4] that fine spray atomizing nozzles give rise to significant air velocities which may aid in extinguishment by blow-off effects which may not be available in practical extinguishment scenarios. In addition, a number of practical problems have been observed in the use of a spray system in the FMRC apparatus[15]. For these reasons the water application mechanism should not employ a spray system. An attractive alternative is the rake-style water application mechanism which has been used in full-scale experiments at FMRC with excellent results[16]. There may be some problems associated with scaling this approach to a small-scale apparatus, but these do not appear to be insurmountable. The rake will need to use very small discharge orifices at close spacing and will need to be located as close to the sample as possible without interfering with the radiant heating.

Figure 1 demonstrated that the suppressibility of materials exposed to water application is characterized by the application rate required at zero external radiant flux, given as C in Figure 1. The change in the required application rate with increasing radiant flux is not a function of the material, but is simply the water application rate needed to absorb the additional energy flux. Since the material suppressibility index, C, is the zero flux intercept, experiments should be carried out at as low a radiant heat flux at which the material is capable of sustained combustion. For materials which are capable of sustained burning at zero incident flux, this is a simple

matter. For materials that require a finite applied flux for sustained burning, it will be necessary to run experiments at a number of incident fluxes to allow reliable extrapolation to zero incident flux. After sufficient experience has been gained with the apparatus, the slope of the curve will be well known, and the number of tests required may be reduced.

Interpretation of the test results for water application is fortuitously straightforward. The required water application rate at zero incident heat flux, C, is the figure of merit for extinguishability of materials by water-based agents. The smaller C is, the more easily the material is extinguished by water application. The C value required for a particular material use can be determined by comparison of the C value with those of traditional materials and by an analysis of the volume of agent readily available for suppression activities relative to the area of material which is involved. The analysis requires an estimate of the most likely maximum radiative flux, which can be developed from flammability data and a hazard analysis for the material.

Flame Extinguishing Agents

For flame agents it is necessary to provide the agent in the "air" stream in a well mixed fashion at known concentrations. This is quite straightforward for gaseous agents like N_2, CO_2, or Halon 1211 or 1301. For dry powder agents, the powder needs to be well dispersed in the "air" stream via a powder feed system. This can be accomplished using a worm gear feeder system similar to that employed by Fisher and Leonard[17]. The actual concentration provided can be determined from the measured air flow rate and the powder feed rate or by collecting the powder near the sample via a filter after extinguishment. It has been demonstrated that the particle size of the agent is extremely important[11,17,18], and that maximum performance is achieved for particles of about 25 μm or less. As such, excellent particle size control is required for correct comparisons of agent effectiveness.

Reignition of a material after agent application is ended is a serious concern, especially for flame agents which do not actively cool the fuel surface directly. As such the time of agent application to prevent reignition is a critical performance aspect of the material and will be a function of the external radiant flux. For very high fluxes, no finite duration will allow sufficient cooling, whereas at lower flux levels it will be possible to prevent reignition. Reignition will be a particularly important consideration for charring materials which support glowing surface combustion.

Interpretation of the test results for flame agents is far more difficult than the fuel surface agents. The characteristic curves (see Figure 7, for example) are decidedly nonlinear and dependent on the material and the agent. Equations 5 and 14 which describe the curves are sufficiently complex that it is not possible to identify simple indices of suppressibility. Nonetheless, there are two experimental conditions of definite interest in characterizing the suppressibility of a material.

For each material/agent pair there is a concentration of agent required to suppress the fire when the material is exposed to very high radiant fluxes. This concentration is the high flux asymptote universally observed in the gas phase agent plots. It is a function of the agent and the reactivity of the fuel volatiles produced from the material. It is not a function of the solid phase response of the material to heat. This asymptotic concentration of agent is the minimum concentration which will suppress the material flame regardless of the radiative environment.

Of equal interest is the concentration of agent required in the absence of external radiation. This involves both the solid and volatile properties of the material. Reconstructing the material response curves from a limited number of experiments may be possible using a curve fitting procedure in conjunction with Equations 5 and 14. This would allow the full performance of the material suppressibility to be assessed and characterized. Additional work will be required to determine the extent to which this is feasible, in particular for agents which act through endothermic decomposition and through chain breaking processes.

CONCLUSIONS

Fire point equation and the models developed here provide a unified framework in which to evaluate the suppressibility of materials and agent effectiveness. The model points out the distinct differences in material suppressibility for agents which cool the material surface and those which act in the gas phase. The model clearly demonstrates the desirable qualities of any new suppression agent. The model can be used directly in identifying candidate suppression agents and provides a method for comparing the effectiveness of new agents relative to existing agents.

Where experimental data is available, the models perform very well. Additional experimental work beyond that currently available in the literature is required to fully validate the models and to provide further modeling guidance, especially for halons and dry chemical agents.

Using the fire point equation and the models developed here, it is possible to evaluate the suppressibility of materials and agent effectiveness by modifying existing small-scale rate of heat release (RHR) test methods. The most promising small-scale RHR test methods are the FMRC Flammability Apparatus and the Cone Calorimeter. The FMRC apparatus would require less modification, since it is already operated as a closed environment system. Some enclosure of the sample in the Cone Calorimeter would be needed to allow gas phase agents to be tested in that apparatus.

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