HALON ALTERNATIVES EXTINGUISHMENT PATHWAYS

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ABSTRACT:

We conducted a study to identify alternatives for Halon 1301 in the mid-70's and concluded there was not any sufficiently efficient clean agent then available, Although we realized that bromine containing compounds could cause ozone recombination similar to chlorine action, we did not consider the ozone depletion potential as a critical weighing factor. International treaty now drives such action. Consequently, we have continued our fire suppression research addressing the new realities.

In addition to looking for acceptable alternatives, we developed a technology base of extinguishant requirements, including requirements for extinguishment mixtures, with a liquid hydrocarbon fuel cup burner. These results, and computer hydrodynamic-chemical modeling, has allowed for separation and quantification of physical and chemical pathways of suppression action. The resulting linear predictive model can be used to calculate the concentration of physical suppression agents required to effect extinguishment, and estimate the requirements for chemically acting agents. It also differentiates the effectiveness of the radical components of the agents. For example, Halon 1301 (CF_3Br) functions 20% as a physical agent, and 80% as a chemical agent, with bromine radical action being 55%, and the CF_3 radical action being 25%. This type of information can be used to propose and evaluate alternatives for Halons 1301 and 1211.

Current results show that while physically acting extinguishants have a constant effectiveness value, the efficiency of chemically acting extinguishants is a function of agent concentration, with Halon 1301 efficiency increasing at lower concentrations. Data from tests employing varying oxygen concentrations have now been interpreted with a revised model based on a "free oxygen" concept.

This paper reviews our linear model development and capabilities, as well as its' generalization and modification to our "free oxygen" model. Improved representation of extinguishment pathways in the models continues with incorporation of thermodynamic and kinetic information to better calculate the importance of chemical action of candidate suppressants.

BACKGROUND:

An understanding of the issues in identifying non-ozone depleting fire extinguishants as replacements for halons requires some knowledge of fire extinguishment processes. This paper is to help serve in giving and using that understanding. In no way should it be regarded as a detailed or complete treatment.

Fires can be suppressed by a number of mechanisms, usually occurring in combinations. The extinguishment pathways listed in Table 1 serve as a convenient framework for discussion.

TABLE 1

EXTINGUISHMENT PATHWAYS

PHYSICAL - NONREACTIVE		CHEMICAL - REACTIVE
ENERGY	SPATIAL	SCAVENGING
HEAT CAPACITY	DILUTION	CATALYTIC
THERMAL CONDUCTIVITY	SEPARATION	THIRD-BODY EFFECTS
DECOMPOSITION	DECOUPLING	IONIC

An organic fuel flame can normally exist only between two temperature limits. The adiabatic flame temperature is the highest temperature to which the reaction exoergicity can heat the product gases. The minimum propagation temperature is the lowest temperature that will allow sufficiently rapid chemical reactions to maintain the flame. When energy loss sinks such as heat capacity or thermal conductivity lower the flame zone temperature below the minimum propagation temperature (approximately 1600 K), reaction rates slow and extinguishment results. Decomposition also requires energy input to break bonds. This mode, but not possible inhibiting reactions of the decomposition products, is usually considered a physical process.

Dilution slows reaction rates by the law of Mass Action. An agent present at 10 percent means dilution of 10 percent. Bimolecular reaction rates are then slowed to 81 percent of their former rate. Separation is the classical concept of physical separation of fuel from oxidizer. A blanket or foam layer are examples. Decreasing energy feedback to unburned fuel reduces fuel vaporization and decomposition. Examples of decoupling of the energy and radical rich zone from the unburned gases are blowing out a candle or blasting out an oil well fire.

Chemical pathways are very efficient and are the primary reason for employing the bromine containing halons. The radical species responsible for flame propagation are directly removed from supporting combustion by establishing alternative reaction paths.

A suppressant that removes one radical acts as a radical scavenger. A species that can remove radicals may be functioning as a catalyst, having a much greater suppressant impact. HBr, formed by bromine combining with a hydrogen atom, can react with a second hydrogen atom to form a much less reactive hydrogen molecule, regenerating the bromine to repeat its chemical suppression action.

Facilitating radical recombinations by acting as a third-body is not as significant. Such interaction could be considered physical as there are no chemical changes involved. The significance of ionic suppression pathways has not been adequately demonstrated.

The molecular reaction

$$H + O_2 \rightarrow OH + O - 16.8 \text{ kcal/mole} \qquad (1)$$

is usually the major oxygen consumption and the primary branching reaction. It is key in flame propagation as one reactive radical generates two reactive radicals. If its' rate is decreased sufficiently, the fire will be extinguished. Dilution (lowering reactant concentrations), energy removal (reducing temperature on an endothermic reaction), and radical removal (chemical scavenging or catalytic reaction) all take place with chemical suppression agents. Any suppressant, by virtue of its mass, possesses physical action. Chemical pathways to various degrees can also be operative. In total flooding applications, separation and decoupling mechanisms are not usually significant.

EXPERIMENTAL:

Our experimental research indicated a model based on heat capacify could be used to predict physical action extinction requirements. To get a better appreciation of the relative contributions of heat capacity, thermal conductivity, and dilution, we (primarily Dr. Doren Indritz) computer modeled atmospheric pressure hydrogen-oxygen-nitrogen combustion using 11 species, 58 reactions, thermodynamic values, temperature dependent rate reactions, and heat and mass transfer for each species. The flammability limit as a function of composition was mapped out and matched experimental values quite well.

We then studied suppression of stoichiometric hydrogen-air mixtures by adding varying amounts of physical agent. By selectively 'turning off' the program subroutines that calculated the heat capacity, thermal diffusion, or dilution effects, we quantified their contribution to achieving flame extinction. Helium effectiveness is due primarily to dilution, with heat capacity effects accounting for only 20 percent. For diatomic nitrogen, heat capacity contributes 50 percent. For polyatomic species, such as CF_4 and SF_6, heat capacity is the dominant extinguishment factor, contributing over 70 percent of the suppression effectiveness.

Laboratory scale fires used a liquid pool diffusion flame burner patterned after the Imperial Chemical Industries and Factory Mutual Research Corporation cup burners. The burner consists of a 2.8 cm tapered pyrex cup in a chimney of 10.5 cm id. Air and agents are mixed and flow up past the liquid fuel fire. Experiments with n-heptane fuel were used for model development, although other fuels, such as 2-propanol, gave similar results.

Agents tested included He, Ne, Ar, N_2, CO_2, CF_4, SF_6, CF_3Cl, CF_3Br, CF_3I, SF_5Cl, SF_5Br, and S_2F_{10}. An experiment consisted of igniting the liquid fuel in flowing air, allowing flame stabilization, and adding agent until the diffusion flame was extinguished. Gas samples taken from the inlet line were analyzed for agent concentration. The agent percentages required to extinguish the heptane pool fires are given in Table 2.

TABLE 2

Agent Concentration (%) Required to Extinguish Heptane and 2-Propanol Pool-Air Diffusion Flames

Agent	Heptane	2-Provanol
Ar	41	--
Ne	37	39
He	32	30
N_2	30	30
CO_2	21	20
CF_4	16	15
SF_6	11	11
CF_3Cl	6.9	--
CF_3Br	3.1	3.2
CF_3I	3.2	--
SF_5Cl	13	--
SF_5Br	4.2	--
S_2F_{10}	10.5	--

MODELING:

We observed that the calculated extinguishing mixture heat capacity when normalized per mole of oxygen was approximately constant for the physically acting agents. Normalizing per mole of oxygen in the gas mixture is valid because the heat of combustion for most hydrocarbon fuels (and many organics) is approximately constant per mole of oxygen consumed. A more rigorous treatment uses $\Delta H'$, the normalized enthalpy of heating. This is the heat capacity as a function of temperature integrated from room temperature up to the minimum propagation temperature of 1600 K, given in equation (2).

$$\Delta H' = \Sigma_i \frac{X_i}{X_{O_2}} \int_{298}^{1600} C_{pi}^I \, dT \qquad (2)$$

where $\Delta H'$ = Mixture Enthalpy of heating per mole O_2

X_i = Mole fraction of component i in the mixture.

C_{pi}^I = Heat capacity of component i at temperature T.

When the heptane data in Table 2 is so treated, the polyatomfcs CF_4 and SF_6 yield $\Delta H'$ values of approximately 64 kcal (mole O_2)$^{-1}$. Equation (2) can be inverted. The mole fraction of new agent A, X(A), required to extinguish an air pool fire can be calculated from its' enthalpy of heating $\int C_{PA} \, dT$ as

$$X(A) = \frac{\Delta H'(0.21) - 7.9}{\int C_{PA} \, dT + \Delta H' (0.21) - 7.9} \qquad (3)$$

The value 7.9 is the enthalpy of heating for nitrogen; 0.21 is the oxygen mole fraction in air. This formalism ignores dilution and thermal conductivity effects. However, any changes between agents are minimized by the large nitrogen concentration in air.

We now define a suppression fraction X^S to be the mole fraction of agent used experimentally, divided by X(A), the mole fraction of that agent required (or predicted) to cause extinguishment.

$$X^S = X(\text{experimental})/X(A) \qquad (4)$$

The extinction index, the sum of individual agent suppression fractions (analogous to the flammability index), is equal to unity at extinguishment.

$$\Sigma_i \, X_i^S = 1 \text{ (At extinguishment)} \qquad (5)$$

The linear additivity of physical action (Eq. (5)) was proven by extinguishment experiments with CF_4 and SF_6 mixtures. This then constitutes our physical action suppressant predictive model.

CHEMICAL MODEL:

Knowing the physical suppression contribution of agents is necessary for evaluating the presence and extent of chemical action. For a first order chemical effectiveness calculation, we assume physical and chemical effects are additive. The suppression fraction, X^s, can then be separated into physical, X^{sp}, and chemical, X^{sc} terms for each species.

$$X^s = X^{sp} + X^{sc} \qquad (6)$$

The suppressant series CF_3Cl, CF_3Br, CF_3I, and SF_5Cl and SF_5Br are of special interest. The halons are known suppressants; the sulfur compounds are their analogs. S_2F_{10} is of interest as it decomposes into two SF_5 radicals. Using a value of **64** kcal (mole O_2)$^{-1}$ in Eq. **(3)** for ΔH^1, we calculate the amount of CF_3Y and SF_5Y agents required. Equations (4), (5), and **(6)** then allow calculation of X^{sc}, the chemical suppression fraction. These values are given in Table 3. X^{sc} values less than zero imply the species acts as a flame promoter rather than as a suppressant.

TABLE 3

Physical and Chemical Suppressant Fraction Values for CF_3Y and SF_5Y

Agent	% Required for Extinauishment	Physical % Prediction	Suppressant Fraction Phvsical	Chemical
CF_3Cl	**6.9**	**15.7**	**.44**	**.56**
CF_3Br	**3.1**	**15.6**	**.20**	**.80**
CF_3I	**3.2**	**15.5**	**.21**	.79
SF_5Cl	**13.**	**10.9**	**1.19**	**- .19**
SF_5Br	**4.2**	**10.9**	**.39**	.61
S_2F_{10}	**10.5**	**6.5**	**1.62**	**- .62**

For the purpose of generating a simple chemical fire suppression model, we assume that since the bond strengths $D(CF_3\text{-}F)$ and $D(SF_5\text{-}F)$ are much greater than any $D(CF_3\text{-}X)$ or $D(SF_5\text{-}X)$ (X = Cl, Br, I), one can assume the C-Cl, C-Br, S-Cl and S-Br bonds are broken while C-F and S-F bonds remain intact. It is not important to the model whether the initial suppressant molecule reaction is an abstraction or dissociation. X^{sc}, the chemical suppressant fraction for agent AB, can be separated into $X^{sc}(A)$ and $X^{sc}(B)$.

Suppression fraction normalized by species mole fraction is called "Suppressant Factor" F^s as:

$$F^s(A) = X^s(A)/X_A \quad (7)$$

Equation (5), the extinction index, can be generalized as a linear sum using equations (6) and (7) as

$$\Sigma_i X_i F^{sp}(i) + \Sigma_i X_i F^{sc}(i) = 1 \quad (8)$$

where: $F^{sp}(i)$, $F^{sc}(i)$ = Suppressant Factor, Physical and Chemical, respectively.

When the sum of agent mole fraction times suppressant factor reaches an extinction index value of one, extinguishment occurs. Although linear additivity may not always be true since different radicals may act via different "bottlenecks," this approximation will be used for the following model.

Solving equation (8) using the data on the chemical agent series in Table 3 as linear equations, we find the suppressant factor values listed in Table 4.

TABLE 4

SUPPRESSANT FACTOR VALUES

Physical		Chemical	
	F^{sp}		F^{sc}
CF_4, CF_3Cl, CF_3Br, CF_3I	6	CF_3	7
SF_6, SF_5Cl, SF_5Br	9	SF_5	-3
S_2F_{10}	15	Cl	1.6
		Br	18
		I	17

These values show the SF_5 radical to be a flame promoter rather than an inhibitor, and that the CF_3 and I radicals are chemical suppressants, with the I radical as powerful as the Br radical. Halon 1301 (CF_3Br) suppression action is 20% physical, 25% chemical due to CF_3, and 55% chemical due to Br. This linear physical and chemical predictive model is applicable to fuel - air systems. Further discussion is in reference 3.

The above model assumes complete chemical interaction. As such, it is simple to use and is instructive. However, this assumption is not always correct. A ligand on an agent molecule may be strongly bound. In that case, the physical predictive model should be valid. If the bond is very weak, or the ligand very reactive, the combined physical and chemical model should be valid. Reality is frequently in the middle ground. The actual suppressant agent concentration required for extinguishment will be bounded by the respective predictions of the above two models. The degree to which chemical action comes into play can be weighted by the likelihood, under flame conditions, of unimolecular decomposition or abstraction reaction. Development of this modified chemical predictive model continues, including incorporation of larger molecules.

NONLINEAR EMPIRICAL CHEMICAL MODEL:

The linear additivity assumption made above is not completely valid for chemical interactions. Mixtures of SF_6, a physical agent, and halon 1301, primarily a chemical agent, show an enhanced efficiency deviation from linearity (See Figure 1).

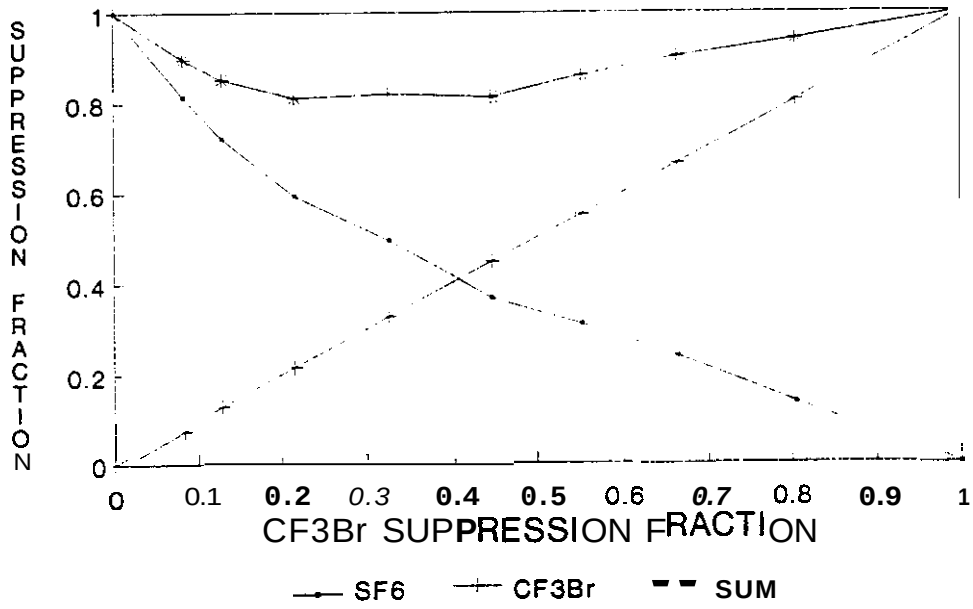

Figure 1. Suppressant mixture effect

Fire extinction is achieved with a suppression fraction sum of less than 1. This enhancement is not synergism, but rather a manifestation of nonlinearity. This can be better understood by reploting the same data showing the suppression fractions for physical and chemical pathways in Figure 2. The actual chemical fraction, unity minus the physical fraction, is shown as greater than the linear model calculated chemical fraction. The ratio of these two functions is shown as the relative efficiency of CF_3Br

chemical suppression as a function of CF_3Br concentration. This is the first demonstration quantitatively showing the variation of suppression efficiency as a function of concentration.

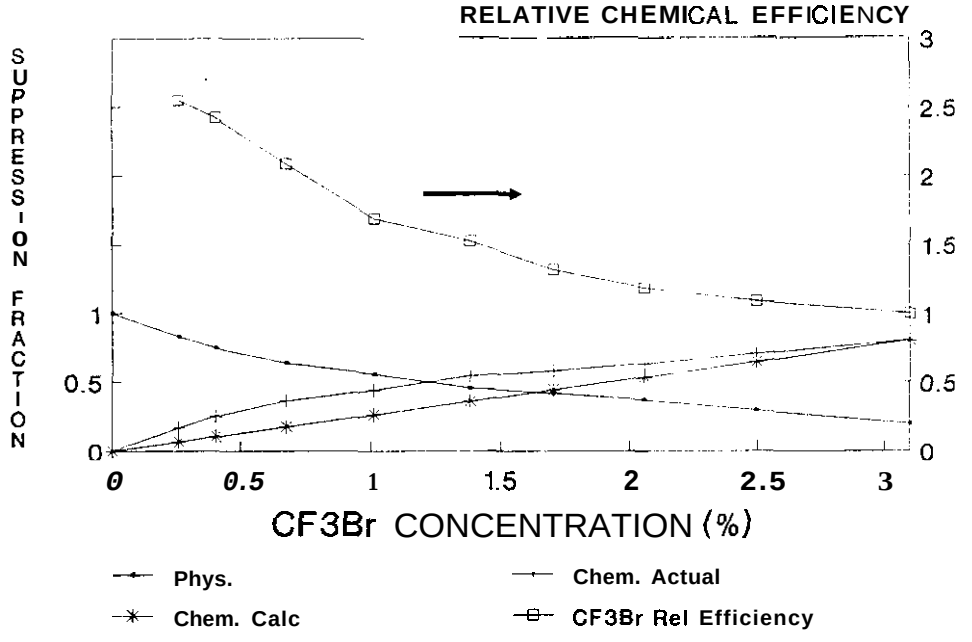

Figure 2. Chemical suppression efficiency

A different formalism is now required. The physical model is based on a suppressant adding at least 26 kcal (mole O_2)$^{-1}$ energy sink from enthalpy of heating in air systems. A more general equivalent criteria is to evaluate the amount of oxygen "neutralized" by the suppressant. This is done by our Free Oxygen model adapted from work by Tucker et al[4].

$$\text{FREE } O_2 = [O_2] - \Sigma_i \left([O_2]_{ext}/[X_i]_{ext}\right) * [X_i] \qquad (9)$$

where $[O_2]$ and $[X_i]$ are mixture oxygen and agent concentrations
$[O_2]_{ext}$ and $[X_i]_{ext}$ are oxygen and agent concentrations at extinguishment, either from experiment or model (physical)

When the calculated concentration of oxygen "canceled out" by all suppressant agents present equals the experimental oxygen concentration, the mixture will not support combustion. The effectiveness of halon 1301, determined as a function of free oxygen in the gas mixture to which it is added, is shown in Figure 3. Data for CF_2BrH (available as Great Lakes FM-100™) are given in Figure 4. The suppression index is an absolute, not relative, figure of merit. A suppression index of 4, for example, means four percent free oxygen concentration is neutralized by one percent agent.

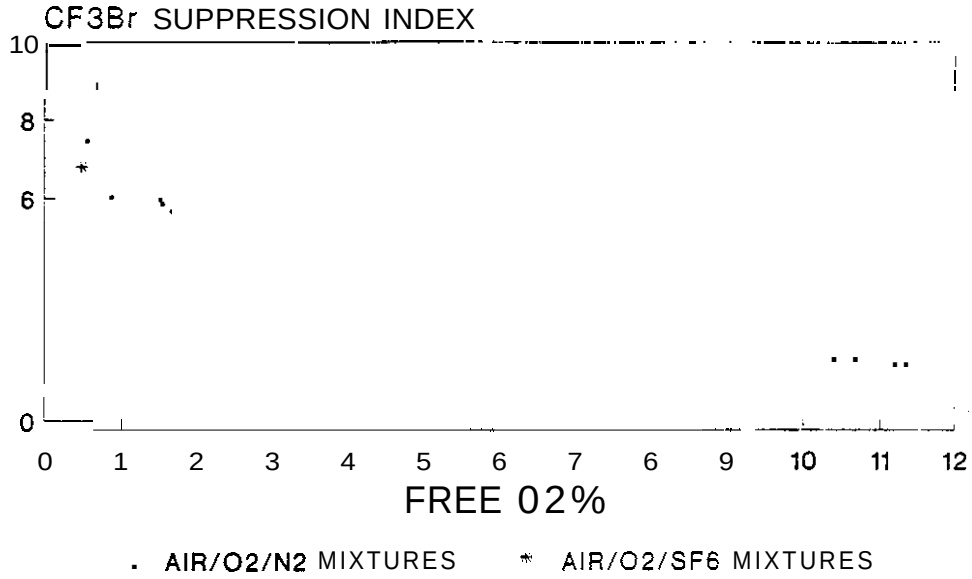

Figure 3. CF_3Br efficiency in Oxygen/Nitrogen/SF_6 gas mixtures

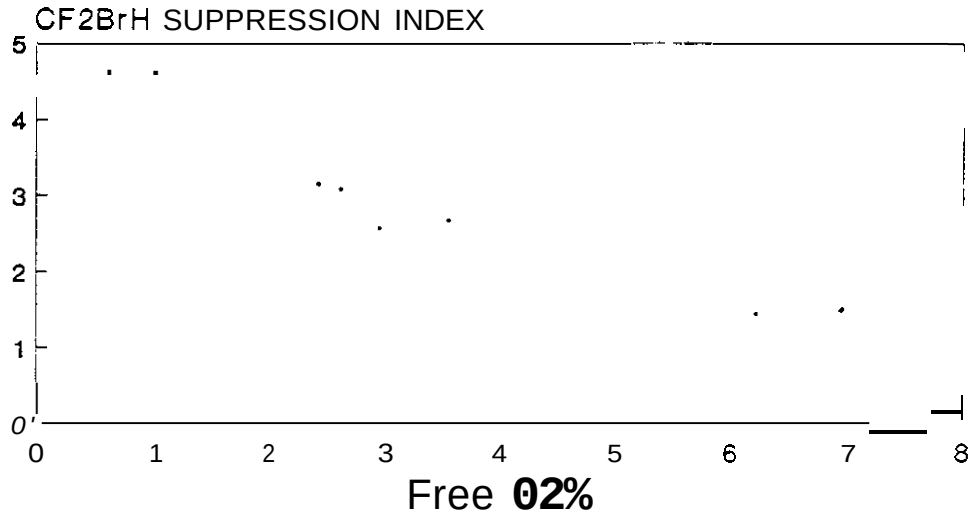

Figure 4. CF_2BrH efficiency in Air/Nitrogen gas mixtures

The nonlinear empirical chemical model can be used to differentiate and characterize chemical suppression activity. Chemical action is manifested by nonlinear behavior; physical action by a constant suppression index. The absolute magnitudes are also different. There is no more limitation to air systems. Depleted or enriched oxygen atmosphere suppression requirements can also be predicted. Another important feature of this nonlinear empirical chemical model is that once initial extinction data have been determined, the model can be used to predict agent requirements for mixtures and blends. Halon replacements can be designed to take advantage of "enhancement" effects, while minimizing stratospheric ozone depletion and toxicity concerns.

Experimental results are required to form the data basis for model prediction. Further development of our flammability computer modeling with more agent chemistry should minimize that requirement, where adequate kinetic data is available.

HALON REPLACEMENTS:

Halons have been the convenient, clean, safe, magic bullets for a vast variety of fire suppression requirements. There will not be a single replacement. Selecting an agent (or agent mixture) for a specific need will depend on the values placed on a compromise matrix. Considerations will include ozone depletion potential (ODP), fire threat, efficiency, weight, volume, toxicity, greenhouse warming potential (GWP), material compatibility, cost, system criticality, and life safety applications.

Designing a suppressant molecule should include the following component considerations:

Molecular size	Physical effectiveness
Fluorine	Effectiveness (if Reactive), Stability
Chlorine	Physical (throwable), Low chemical action
Bromine	High chemical effectiveness
Iodine	High chemical effectiveness, toxicity ?
Hydrogen UV absorption Reactive bonds	Atmospheric lifetime reduction

Modeling and laboratory scale experiments are very valuable. Their validity for full scale fires must still be demonstrated. We have conducted halon extinguishment tests with cup burners, small compartments, on through 23,000 cubic foot chambers. Future plans include total flooding tests of halon replacements in a 2000 cubic foot compartment, and on our 457 foot fire test facility ship, the EX-USS SHADWELL.

CONCLUSIONS:

Several different fire extinction models, based on how they incorporate the various suppression pathways, have been generated for predicting agent concentrations required for extinguishing fires. They are not exclusive and can serve different purposes. The modified linear physical and chemical model can predict agent concentrations for fires in air while requiring only an approximation of agent heat capacity. The nonlinear chemical model requires one experimental data set, but can then predict concentration requirements for agent blends and for varying oxygen concentrations.

The fire extinction models can be used to help orient the search for halon replacements. Model basis sets can be expanded to include new classes of suppressants. The models also aid understanding suppression phenomena and give insight into the importance of specific inhibition reactions. In particular, they allow the differentiation and quantification of physical and chemical effectiveness, including effectiveness as a function of concentration.

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