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### SURVEY OF VAPOR PHASE CHEMICAL AGENTS FOR COMBUSTION SUPPRESSION

By E. T. McHale

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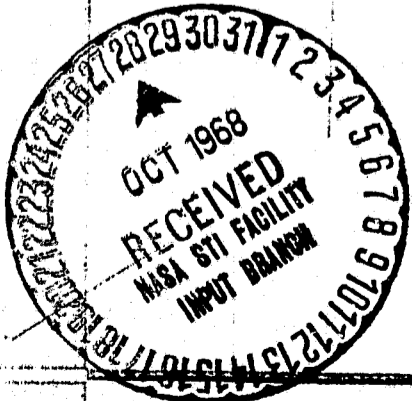
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## INTRODUCTION

A review of the literature of combustion suppression at the present time can rely heavily on previous surveys to provide coverage up to late 1966. For the past eleven years, ever since a comprehensive survey by Friedman and Levy (1), thorough reviewing of inhibition literature has continued by competent workers in the field. The first seven references of this report list these surveys in chronological order. Friedman and Levy summarized the work to 1957 and then added two supplements to the original in the next two years (2,3). Skinner (4) thoroughly covered the following two years in a survey intended to continue the previous three reports, and likewise added supplements in 1962 and 1964 (5,6). In 1966 Fristrom (7) compiled a review of inhibition literature in the same vein as those just mentioned. He brought to the task the credential that he is editor of Fire Research Abstracts and Reviews (FRAR). This publication is a repository of abstracts of literature dealing with combustion suppression, from basic research on flames to fire fighting. Also in 1961 and 1964 Berl (8,9) compiled reviews of fire research. With the exception of references 8 and 9, the cited reviews have emphasized coverage of laboratory-scale research on combustion suppression. Less attention has been given to studies of larger-scale fires in these publications.

In view of these exhaustive surveys, the task of reviewing the literature prior to 1966 is greatly lightened. The indicated approach to a survey, therefore, is to selectively review certain important publications of earlier years to provide background and to obtain understanding of flame inhibitions. Approximately 40 publications falling into this category have been critically reviewed. There also has been thorough coverage of the literature of combustion suppression of the past two years. It develops, however, that since 1966 there has been a large decline in the number of papers dealing with basic inhibition studies. The emphasis has turned to study of the structure of flames containing inhibitors, which approach promises to provide important understanding of inhibition processes.

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The principal sources for this review, in addition to the cited publications, have been Fire Research Abstracts and Reviews, Combustion and Flame, the Combustion Symposia volumes, various types of government and industrial reports, and two machine searches provided by NASA and by DOD.

The scope of the review is limited to chemical suppressants, both homogeneous and heterogeneous, acting mainly on hydrocarbon or hydrogen flames with air or oxygen. Inhibition by purely physical action such as smothering or cooling is not dealt with as such. Studies of both premixed and diffusion flames are included. The types of measurements used to evaluate inhibitor effectiveness are considered, and possible chemical reaction mechanisms by which they act are discussed. Appended to the report are lists of chemical inhibitors and their reported effectiveness. While the emphasis is on fundamental studies, consideration has also been given to application of principles to practical fire control. A discussion is included on requirements of suppressants for flight vehicles.

#### METHODS OF DETERMINING INHIBITOR EFFECTIVENESS

The terms inhibitor and suppressant are used synonymously and can, but do not always, imply extinguishment. They seem to connote a stronger effect than retardant. Friedman and Levy (1) have defined an inhibitor as a substance which makes it more difficult for a flame to burn. Inert additives such as argon, then, are inhibitors. However, only those substances which inhibit by chemical action in the combustion wave are considered in this report. The effect is manifest by a change in a flame property such as burning velocity or flammability limits.

It hardly needs to be established in this survey that certain substances act chemically to suppress combustion, but it is instructive to consider two examples: 1) many covalent halides are strong suppressants, and 6.1 percent of  $\text{CF}_3\text{Br}$  added to a n-heptane-air mixture of any composition will prevent propagation (10). The Br atom has the key role since it takes 26 percent of  $\text{CF}_4$  to cause extinction of the same flame; 2) trace amounts of certain substances such as the inflammable iron pentacarbonyl,  $\text{Fe}(\text{CO})_5$ , exhibit a powerful inhibiting effect on hydrocarbon flames, the burning velocity of a n-hexane-air flame being reduced 30 percent for a 0.017 percent addition. These pronounced inhibiting effects can only be accounted for on chemical grounds, and in later sections they are dealt with and possible reaction mechanisms are discussed. However, besides demonstrating chemical suppression,

the above examples are meant to bring up the question of just how these effects are measured.

In general there are three principal methods used to measure and study inhibition of flames. These are the determination of: 1) the narrowing of the flammability limits; 2) the reduction in burning velocity (both apply to premixed flames); and 3) the influence on diffusion flames. Taking each in order, a common and meaningful way in which to measure suppression effects is by mapping the composition flammability limits for mixtures which contain various amounts of added inhibitor. In a diagram of percent fuel as abscissa versus percent inhibitor, the limits will close in with increasing additive and the curve will go through a maximum. This maximum is commonly called the peak percentage, and represents the amount of inhibitor necessary to prevent propagation for any composition. The method was used to obtain the data of Table I in the appendix, and in many other publications, for example references 12, 13 and 14. A technical point should be mentioned in regard to flammability limits. They can depend on the dimensions of the apparatus, i.e. burner, and this parameter is usually neglected. It could be important when scaling predictions are attempted. As an example of such a type of discrepancy, it was found that the amount of  $AlCl_3$  vapor needed to extinguish methane-air flames differed by a factor of 2 in two independent studies (15, 16). The difference was attributed by Friedman and Levy (15) to the different apparatus and ignition sources.

Another common method to evaluate inhibiting effects is by measuring the burning velocity. Such experiments are usually performed in open-tube burners, as flammability tests often are. The velocity method has the disadvantage that usually the extinction conditions are not determined. The results are reported as the amount of additive needed to reduce the velocity by a certain amount. This method was used to obtain the data of Table III and in other publications (11, 17).

Next, the measurement of suppressing influence of chemical additives on diffusion flames is considered. The rationale for studying inhibitors in a diffusion system is that it more closely approximates real fire situations. Against this must be weighed the complicating factors of diffusion flames which are, for purposes here: 1) no measurable fundamental property such as burning velocity, and 2) dependence of inhibiting effect on streaming velocity. These objections are serious for annular or flat diffusion flame burners.

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Nevertheless, some useful studies have been carried out using these types (18, 19). There is another burner which is a great improvement for diffusion flame studies. This is the opposed-jet burner (20) which consists of two coaxially-opposed tubes through which fuel and oxidant flow, meeting in a space between and forming a diffusion flame. The aforementioned objections are substantially overcome by the opposed-jet system. In this type of burner, as the streaming velocities are increased, a point is reached at which an opening appears in the center of the flame. This opening is reproducible and represents the point at which mixing rate of reactants exceeds the chemical reaction rate. It provides a convenient parameter, referred to as apparent flame strength, to use to evaluate effectiveness of inhibitors; the stronger the inhibitor the lower the flow velocity at which the flame "breaks." Two investigations have been reported in which this technique was used to study inhibition (21, 22).

Actually there is one other method which should be mentioned. This is the determination of quenching distances for inhibited premixed flames (23, 24); however, it is rarely used.

#### CHEMICAL INHIBITORS

Chemical additives are usually categorized as homogeneous or heterogeneous inhibitors depending upon whether they enter the flame as vapor or solid, respectively. They are believed to act to suppress combustion by scavenging active chain carriers early in the combustion wave. However, vapors may not necessarily act to suppress combustion by entering into homogeneous chemical reactions; and solids may not act via heterogeneous reactions. Consider some examples to clarify this. Compounds such as the alkyl halides which are gaseous inhibitors, certainly react homogeneously; further analysis of this is given later. Solid additives, e.g.  $\text{KHCO}_3$ , may act heterogeneously by providing surface for radical deactivation. Alternately, solids may gasify in the flame and their vapors may then be the principal inhibiting species, acting homogeneously (25). Conversely some compounds, e.g. tetraethyllead, titanium tetrachloride, iron pentacarbonyl, which are vapor as they enter flames, may be reduced or oxidized to the metals or metal oxides and these species could actually be the retarding agents (11). The mode of action of many chemicals is obscure, and there may be no fundamental basis for the usual classification. Nevertheless it is a useful breakdown, properly qualified, and will be used below.

### Homogeneous Inhibitors

The alkyl halides are the most common fire suppressants of this class and have received the most study. Table I of the appendix (10) lists 56 compounds, mostly alkyl halides, which have been tested as inhibitors and ranked in decreasing order of effectiveness. Other studies in which several such chemicals have been investigated include (11, 17, 24) although not nearly so many were tested.

Several points and generalizations can be made in regard to these halogen-containing compounds. Three very common inhibitors,  $\text{CH}_2\text{ClBr}$  (commonly called CB),  $\text{CH}_3\text{Br}$  and  $\text{HBr}$ , are roughly in the middle of the list of Table I.  $\text{CF}_3\text{Br}$ , a "Freon" fire suppressant, is somewhat better than CB.  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ ,  $\text{C}_4\text{F}_{10}$  and  $\text{C}_7\text{F}_{16}$ , which are not believed to display any chemical action in suppressing combustion, rank in the order expected on the basis of their heat capacities. The following tabulation compares inhibitors on the basis of the type of halogen (peak percentage listed on right).

$\text{CF}_4$	26
$\text{CF}_3\text{Cl}$	12.3
$\text{CF}_3\text{Br}$	6.1
$\text{CF}_3\text{I}$	6.8

The ranking as given is in the expected order of decreasing strength of the  $\text{CF}_3\text{-X}$  bond, excepting for the iodine which is comparable to the bromine compound. Similarly, ethyl bromide and iodide are approximately equal in effectiveness, but  $\text{CH}_3\text{I}$  is significantly better than  $\text{CH}_3\text{Br}$ . Rosser, Wise and Miller (917) observed an excellent correlation between inhibitor effectiveness and number of bromine atoms per molecule. The rate of flame speed reduction increased linearly with increasing Br content of a number of methane-derivative inhibitors plus  $\text{Br}_2$  and  $\text{HBr}$ . However, such a correlation is poor in the Purdue list (10) as the first four items on the list attest. There is also no similar relation for any of the other halogens.

The preceding deals with additives which cause the extinction of premixed flames as distinguished from some lesser inhibiting effect. In general, relatively large amounts of chemical inhibitors must be added to completely prevent deflagration, which raises the question of their cooling effect. For example,  $\text{Br}_2$  is probably the most effective extinguishant, but this has a peak percentage of ~1.5% in the n-hexane-air system (11) and ~2.5%

in methane-air (12). The peaks in these two systems occur at 3 and 9% fuel, respectively. Thus the amount of added inhibitor is quite high relative to the amount of fuel, and even higher in the case of substances other than bromine. No doubt the additives that extinguish act to some extent as flame-temperature depressants. There is a paucity of data on this aspect of inhibition, but one study has yielded some interesting results. Simmons and Wolfard (18) have calculated the temperatures for stoichiometric  $\text{CH}_4$ - and  $\text{C}_2\text{H}_6$ -air flames with and without the peak concentration of  $\text{Br}_2$ , and these are shown below:

<u>Hydrocarbon</u>	<u>Flame Temperature</u>	
	<u>Without <math>\text{Br}_2</math></u>	<u>With <math>\text{Br}_2</math></u>
$\text{CH}_4$	2224°K	2117°K
$\text{C}_2\text{H}_6$	2263°K	2172°K

The peak concentrations occur very near stoichiometric. Addition of bromine lowers the flame temperatures somewhat, however, the temperature of the normal limit mixtures in the absence of  $\text{Br}_2$  is 1550°K. Clearly, in the  $\text{Br}_2$  case at least, the temperature depressing effect is secondary. One would guess that it might not be in the case of, say,  $\text{CF}_3\text{Br}$  inhibiting heptane flames.

In this report chemical additives are considered on a gas volume basis. Low molecular weight agents, however, have an advantage when considered on a weight basis, and weight or liquid volume may be the proper basis for certain fire control applications. Thus water, a physical extinguishant with a molecular weight of 18, emerges as superior to many chemical extinguishants if only weight is considered. It is much less attractive on a liquid volume basis since its density is much below halogenated organic compounds. Also its high heat of vaporization and the necessity of delivering such a high molar quantity to the site of a fire offset its weight advantage.

There are compounds which produce strong inhibiting effects when added in much smaller amounts than those so far considered. Many of these substances will not cause extinguishment but they will retard combustion. The most familiar example would be the use of tetraethyllead in preventing engine knock, ~0.2 percent being effective. Lask and Wagner (11) have examined the effect of a great variety of additives on a n-hexane-air flame. These comprise volatile inorganic substances and are collected in Table II of the appendix together with the percent of each needed to reduce the burning velocity by 30



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percent. The first seven compounds are listed for comparison. The majority of the additives are halogenated and as can be seen from the list, some are no more effective than alkyl halides while others are roughly five times as effective. It would have been desirable to have included a brominated fluoro-alkyl for comparison, although presumably about 1% of such an additive would be required. The last three members of the list show extraordinary retarding ability and are effective in quantities of an order of magnitude lower than the other candidates. It is noted that most of the substances listed in Table II are based on elements in groups IIIA to VIA of the periodic chart. Examination of the list along these lines, however, does not disclose any consistent trends.

The influence of chemical inhibitors on diffusion flames requires separate discussion. Simmons and Wolfhard (18) made a study of inhibition of hydrocarbon-air flames by methyl bromide using a flat diffusion flame burner. They made the discovery that approximately an order of magnitude more  $\text{CH}_3\text{Br}$  must be added to the fuel gas stream than to the air stream to effect extinction. The amount added to the air is of the same order as that for premixed flames. The explanation is that in the diffusion flame reaction zone the reactants are present in stoichiometric proportions. For  $\text{CH}_4/\text{air}$ , for example, this ratio is approximately 1/9, which means that 9 times as much air as fuel will diffuse into the flame. It will bring with it 9 times as much inhibitor as the fuel will. Hence, when inhibitor is in the fuel it needs to be present in large excess to diffuse into the flame in sufficient quantity to prevent propagation. It was also noted that a separate  $\text{CH}_3\text{Br}$ -air flame was established adjacent to the main diffusion flame. These observations with  $\text{CH}_3\text{Br}$  were borne out by Creitz (19) who also examined the effect of  $\text{CF}_3\text{Br}$  on diffusion flames of hydrocarbons. Similarly  $\text{CF}_3\text{Br}$  must be present in the fuel stream in large excess over that in the air stream.

One other study of diffusion flame inhibition must be considered. Friedman and Levy (21) measured the "breaking point" of inhibited  $\text{CH}_4$ -air flames in an opposed-jet burner. The ranking of the inhibitors they tested is  $\text{CH}_3\text{Cl} < \text{CCl}_4 < \text{CH}_3\text{Br} \approx \text{CF}_3\text{Br}$ , which is in reasonable agreement with premixed flame results.

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Lastly, in connection with homogeneous inhibition, the publication of Miller, et al. (26) should be mentioned. A large number of substances -- hydrocarbons, organic and inorganic halides, and other types of compounds -- were screened for suppressing effect on premixed H<sub>2</sub>-air flames. The listing is too extensive to be included in this survey, but for anyone studying H<sub>2</sub> flames it would provide a good guide to what effect a variety of additives have on the burning velocity.

#### Heterogeneous Inhibitors

As with homogeneous inhibitors, a great variety of salts and other powders have been tested for their suppression effect on flames. The alkali metal salts in particular exhibit extinguishment power and have been extensively studied, especially the carbonate, oxalate and halide compounds. The chemical nature of the solid determines the strength of the suppressing effect to an extent, but a property of equal importance is the surface area. These two topics will be discussed in order.

There have been a number of studies reported in which quite a few powders have been investigated in each (16, 25, 27-32). There is difficulty comparing the results of different investigations because of the non-uniformity of data reporting. The work of Friedrich (31) can serve fairly well to illustrate the role of the chemical nature of the solid. Powder of 44 $\mu$  particles was dispersed, using a screen, as a dust cloud into diffusion flames of H<sub>2</sub>, CO, and illuminating gas. The choice of this study has the disadvantage that the work was not carried out by a highly controllable technique, but a great many substances were tested. Considering only the results for illuminating gas, the carbonates of the alkali metals were roughly twice as effective as the halides. Although the data are somewhat inconclusive, it appears that wet oxalates are an order of magnitude better than carbonates. This same study shows that the bicarbonates of Na and K are less effective than the carbonates, which observation is generally supported in references 25 and 28. Of these two bicarbonates, which are widely used in extinguishing fires, KHCO<sub>3</sub> is the better (see also 25, 32, 33).

The order of effectiveness within the alkali metal series is Li < Na < K as established in the older literature (see 1). The study of Friedrich (31) is in agreement with this ranking although he finds Li compounds to be only slightly less effective than those of Na. Furthermore, rubidium compounds are better than potassium, but the trend fails with cesium which shows

poorer suppressing power. The point must be made that the actual alkali-metal atoms themselves play no role in the inhibition process. Friedman and Levy (21) have added Na and K vapor to methane-air flames and found no effect on flame strength.

To illustrate the importance of surface area of the powdered inhibitors, data from the work of Dolan and Dempster (27) can be cited. In this study, methane-air mixtures were ignited in open-end tubes and suppression- and quenching points were determined. These represented the amount of inhibitor dust necessary to prevent ignition (suppression point) and to prevent the flame from propagating the full length of the tube (quenching point). Larger amounts of powder were required to suppress than to quench; data on quenching are shown below for  $\text{NaHCO}_3$  powder covering a threefold variation in weight added.

Specific Surface Area ( $\text{cm}^2/\text{g}$ )	Quenching Point	
	(g/liter)	( $\text{cm}^2/\text{liter}$ )
11,500	0.046	0.53
9,600	0.112	0.52
3,200	0.158	0.51

The dependence of the quenching point on surface area is brought out very clearly in these data.

Many of the studies were carried out to try to elucidate the role of salts and other solids in suppressing combustion. Some thought has been given to this problem and it is worthwhile to briefly review some points. The chemical role of solids is undoubtedly to destroy active chain carriers and this can be accomplished in one of two ways. The active species may combine on the particle surface or the solid may vaporize in the flame and gaseous product act as the inhibiting agent. The surface area dependence is consistent with both modes of inhibition. Rosser, et al. (25) favor the latter and have calculated that significant evaporation of effective solid inhibitor will occur in the flame. They also report, based on collision calculations of radicals with the particle surfaces, that the solids theoretically cannot be as efficient as they are found to be experimentally if they simply act by providing recombination surface. There has been considerable speculation on chemical reaction mechanisms of inhibition assuming that gaseous species from the solids are the inhibiting agents (1, 21, 25).

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In favor of the alternative mode of inhibition, i.e., radical combination on solid surface, certain points are noted. First, the above collision calculations have been questioned (7). Also it is well known that coating reaction vessels with certain nonvolatile salts, KCl for example, raises the first explosion-limit of the  $H_2-O_2$  system. It is intuitive to suppose that the same role of surface destruction of radicals or atoms is played by solids in hydrocarbon flames. It is also noted that chemical inhibitors of any kind must act in the early part of a combustion wave. Accordingly, solids would have to show appreciable vaporization rates at ignition-temperature levels if their mode of inhibition is by gaseous agents. As has been previously mentioned, Lask and Wagner (11) have observed luminous particles originating in the reaction zone when, for example  $TiCl_4$  vapor had been added to flames. Vree and Miller (34), in a study of ions and spectra of a low-pressure  $CH_4$  flame inhibited with  $Fe(CO)_5$ , have observed emissions from atomic Fe, FeO and a continuum attributed to hot particles in the upstream region of the flame. They interpreted their results as indicative that inhibition by volatile metallic compounds proceeds via very small particles formed in the cooler regions of the flame.

In favor of neither mechanism of inhibition, but germane to the subject is a calculation of Dolan and Dempster (27) who have shown that solid additives lower the flame temperature a great deal. Typically, enough of an alkali halide to suppress combustion will lower the temperature of a  $CH_4$ -air flame from  $\sim 1800$  to  $1500^\circ C$ . The flame temperature at the flammability limit for the uninhibited mixture is  $1300^\circ C$ .

#### STRUCTURE AND CHEMICAL REACTION MECHANISM OF INHIBITED FLAMES

Two topics which are integral parts of the inhibition picture have received attention: 1) microstructure of flames containing inhibitors; and 2) postulated inhibition reactions and how they obstruct the normal reaction pathways. The discussion is limited to hydrocarbon flames inhibited with volatile halogen-containing additives.

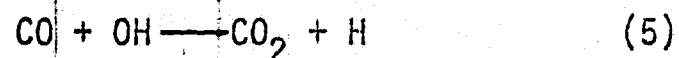
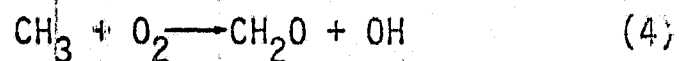
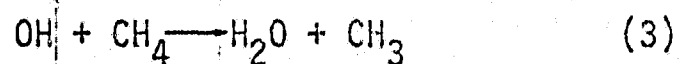
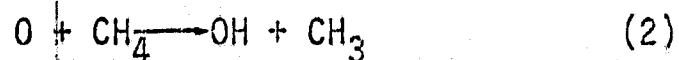
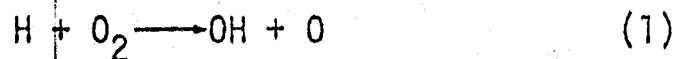
There are three elements which constitute the microstructure of a flame: the aerodynamic flow field; the temperature profile; and the composition profiles of the chemical species through the wave. The determination and interpretation of these are described in reference 35 and 36. Several groups have made contributions in the area of structure of inhibited flames, notably Levy et al. (37), Fenimore and Jones (38-40), and Wilson and Fristrom (41, 42). This approach to the study of combustion suppression holds promise of providing

understanding of the fundamental processes of inhibition.

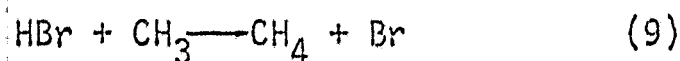
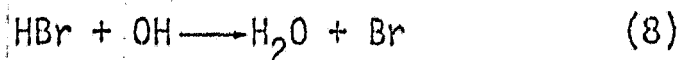
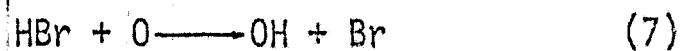
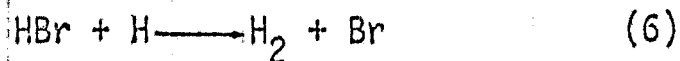
The composition profiles are obtained using quartz microprobes and these are the most valuable data. When properly analyzed by separating the diffusion and chemical reaction components, they yield the reaction rates of various species through the flame. As an example, consider a few pertinent results for a  $\text{CH}_4\text{-O}_2$  flame inhibited with HBr (42).  $\text{CH}_3\text{Br}$  was found to have been formed in the early part of the flame. The profile of the net reaction rate of  $\text{CH}_4$  was shifted to a higher temperature region than in the uninhibited flame. It was sharper and narrower and the effect was more pronounced for HBr than for the less effective inhibitor HCl. These results demonstrate that the inhibition must be impeding chain reactions in the lower temperature part of the flame where these reactions normally begin to become rapid. In the inhibited flame, the ignition temperature is thus raised. The authors describe the inhibited flame as consisting of four zones -- preheat, inhibition, primary reaction, and the post-flame region (in which CO conversion occurs and radicals recombine).

The chemical reaction mechanism of inhibition is not known with certainty, but the important reactions of hydrocarbon and hydrogen flames are known (43); hence, it can be postulated how inhibitors might interfere with them. This has been done by several authors (4, 17, 38, 41, 44, 45) and the following is a brief summary of how brominated additives could react using  $\text{CH}_4$  as an example.

The active species in this flame are H, O, OH, and  $\text{CH}_3$  and some chain and chain-branching reactions are:

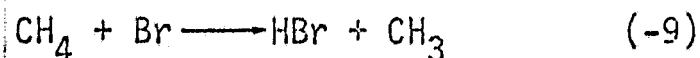


Reaction (3) is believed to account mainly for the disappearance of fuel. Reaction (5) is the principal route to  $\text{CO}_2$  production, the CO arising from  $\text{CH}_2\text{O}$ . Inhibition presumably can be effected by HBr if it reacts with H, O, OH, or  $\text{CH}_3$  via:



Any of these reactions might hinder the normal flame propagating mechanism.

The fate of the bromine atom in the above reactions has been considered. This is equivalent to the problem of how  $\text{Br}_2$  or other brominated additives inhibit flames, since these are believed to act by first decomposing to yield Br. Rosser et al. (17) suggest that once Br is formed it reacts by

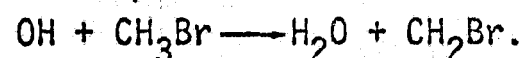


which is the reverse of reaction 9. It is hard to see how this reaction could then lead to hindrance of the mechanism if (7) or (8) were the important inhibiting reaction. For example, the couple (-9) and (8) have the effect of producing one  $\text{CH}_3$  radical for each OH inactivated, but the main role of each OH is to react with  $\text{CH}_4$  to produce one  $\text{CH}_3$  anyway (reaction 3). A similar condition exists with the couple (-9) and (7) and reaction (2). Thus, it would appear that if (-9) is an important part of the inhibition reaction sequence for bromine-containing compounds other than HBr, it must act either coupled to (6) to suppress reaction (1) or by interfering with some reactions other than (2) and (3), possibly reaction (5). Both these possibilities seem remote since reactions (1) and (5) are less important than (3) in driving the combustion. Also if inhibition is principally by impeding reaction (1) it seems more reasonable that it would occur in the same way as it is believed to in the  $\text{H}_2$ -air flame (38); that is, directly by



However, this would require that  $\text{CF}_3\text{Br}$ ,  $\text{CH}_3\text{Br}$ , and  $\text{CH}_4$  be equally effective inhibitors as they are for  $\text{H}_2$ -air (26).

The reactions of homogeneous chemical inhibitors are certainly very obscure. An alternative reaction suggested by Wilson (41) is simply



This has the advantage that it destroys a key radical, OH, but it does not explain why, for example, CH<sub>3</sub>Br is more effective than CH<sub>3</sub>Cl, nor can it be generalized to include CF<sub>3</sub>Br. It is interesting to note that it is an unsettled question whether in fact [OH] is increased or decreased in inhibited flames (17, 41, 42).

#### CONSIDERATIONS IN PRACTICAL FIRE CONTROL, AND REQUIREMENTS OF SUPPRESSANTS FOR FLIGHT VEHICLES

Laboratory-scale experiments conducted on burner flames are chosen by scientists for study because of their reproducibility and manageability and because they offer the most ideal system in which to discover general principles. It is a fact that inhibitors that are effective in flame studies are also effective on fires. There are problems involved in scaling and applying results to practical fires, however, not the least of which is the fact that usually solid or liquid materials are involved as the combustible rather than fuel gas. This immediately introduces a gasification step into the process, which may in fact be the rate limiting step. Fenimore and coworkers (46-48) have reported studies of materials flammability and the inhibition thereof. A recent meeting of the Eastern Section of the Combustion Institute dealt with this topic extensively (49).

It may sometimes be possible to take advantage of this gasification step for suppression purposes. The combustion of most materials occurs in a stable diffusion flame above the material surface. Heat from the flame is transmitted back to the condensed phase causing vaporization. The vapors enter the flame, react exothermically, and continue the cycle. In addition to inhibiting combustion in the flame zone, the material itself can be treated to suppress its vaporization rate or render its pyrolysis products less flammable. For example, chlorinating polyethylene makes it much less flammable by suppressing its vaporization (47).

Similarly, the ignitability of material offers another parameter to attack in attempting to desensitize. A bibliography on ignition is given in reference 9, but special mention may be made of the studies of Simms (50) and Broido and Martin (51). A simplified description of the ignition process is helpful in seeing how to approach the problem of reducing flammability from this standpoint.

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A combustible is brought to a state of steady burning by application of energy, either thermal or radiant. The energy must be supplied for a certain time and at a certain flux level until the temperature gradient within the material reaches that which is present during steady burning. When the surface temperature reaches approximately the steady-state value gasification occurs at an appreciable rate. It is noted that the delivered flux must produce a temperature gradient as steep as or less steep than that of steady burning -- if a steeper profile is present, a flash may result but no self-sustaining combustion will be obtained. The time for the heat buildup in the material is known as the ignition time and is determinable from the thermal properties of the material and the known flux. Whether ignition will actually occur depends upon whether the gas products that emerge from the material at the surface temperature produce a hypergolic mixture with the atmosphere. If they do or if the ignition flux is by a high-temperature thermal source, a steady diffusion flame will develop (if appreciable condensed-phase heat release or adsorption occurs, the foregoing is an oversimplified description). As can be imagined, additives that inhibit the gasification or the flame reactions may be effective in suppressing ignition as well as steady burning. However, one important point is brought out by the work of Broido and Martin (51) in their study of the effect of  $\text{KHCO}_3$  added to cellulose. This is that substances added to materials which inhibit the flame reactions may act as catalysts of the pyrolysis process.

The rate of flame spread over surfaces is another process of importance in fires. This subject has been reviewed (52), and in addition to the obvious properties of a material such as chemical composition, the following variables can be listed as exerting dominant effects in certain situations: moisture content; roughness of surface and edges; orientation of material (for example, flame propagating up or down a sample); size of sample. In addition, heat transfer by convection and radiation in larger scale fires can exert a most important influence which may be absent in laboratory studies. These affect not only flame spread but all other aspects of post-ignition combustibility including suppression.

The foregoing is intended to highlight some of the considerations involved in fire control. In what follows, the requirements for a fire suppressant for flight vehicles are briefly discussed. For military aircraft,



especially relatively high temperatures are often encountered. Omitting consideration of the means of containing suppressant, the high temperature condition imposes the specifications of thermal stability on the inhibitor. Secondly, its vapor pressure at high temperature cannot be prohibitive. Other requirements are low toxicity (and low pyrolyzed toxicity), low corrosibility, nonconduction of electricity, etc. These are discussed in references 53-56. In meeting these requirements, it is desirable not to compromise certain low temperature properties such as freezing point, viscosity, etc., but obviously some trade-off will always be necessary. Workers at National Engineering Science Company have evaluated a variety of halogenated compounds for possible use as extinguishing agents for the Supersonic Transport. The list of these substances, 34 in all, is presented in Table III of the appendix. Ten were found to meet specifications similar to those mentioned above and these are listed in order of decreasing inhibiting effectiveness. The first six of these ten have suppressing strengths approximately equal to  $\text{CH}_2\text{ClBr}$  as measured by the authors; the remaining four are about half as effective as  $\text{CB}$ . Twenty-four were found not suitable and these are indicated in the table with the reason for rejection. Poor thermal stability is a principal reason many of the substances were unsuitable. To meet this requirement a compound had to be thermally stable at  $350^\circ\text{F}$  for 18 hours under the conditions of the test.

The same group at NESC has carried out an interesting study (57) attempting to obtain synergistic enhancement of halogenated inhibitors by adding certain radical initiators. They report the effect to be marginal or nonexistent for the systems they investigated. In another study Barduhn, et al. (58) attempted to adsorb halogenated agents onto powders. The powders were carbon, alumina, silica gel, etc., which are not used as fire suppressants by themselves. They found that carbon with adsorbed  $\text{CF}_3\text{Br}$  is as effective as commercial bicarbonate powder. The possibility suggests itself of adsorbing alkyl halides onto normal flame inhibiting powders.

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Table I

Extinguishing Effectiveness of Agents Evaluated  
in Reference 10. Experimental Conditions: n-Heptane-  
Air Mixture with Flame Propagation through Tube at  
Room Temperature and 300-500 Torr Pressure

<u>Compound Formula</u>	<u>Compound Name</u>	<u>Peak Percentage</u>
$\text{CBr}_2\text{F}_2$	Dibromodifluoromethane	4.2
$\text{CBr}_3\text{F}$	Tribromofluoromethane	4.3
$\text{CF}_3\text{CHBrCH}_3$	2-Bromo-1,1,1-trifluoro-propane	4.9
$\text{CBrF}_2\text{CBrF}_2$	1,2-Dibromotetrafluoroethane	4.9
$\text{CF}_2\text{ICF}_2\text{I}$	Tetrafluoro-1,2-diiodoethane	5.0
$\text{CH}_2\text{Br}_2$	Dibromomethane	5.2
$\text{CF}_3\text{CF}_2\text{I}$	Pentafluoroiodoethane	5.3
$\text{CF}_3\text{CH}_2\text{CH}_2\text{Br}$	3-Bromo-1,1,1-trifluoropropane	5.4
$\text{CH}_3\text{CH}_2\text{I}$	Ethyl iodide	5.6
$\text{CF}_3\text{CF}_2\text{Br}$	Bromopentafluoroethane	6.1
$\text{CH}_3\text{I}$	Methyl iodide	6.1
$\text{CBrF}_3$	Bromotrifluoromethane	6.1
$\text{CH}_3\text{CH}_2\text{Br}$	Ethyl Bromide	6.2
$\text{CH}_2\text{BrCF}_2\text{CH}_3$	1-Bromo-2,2-difluoropropane	6.3
$\text{CClF}_2\text{CHBrCH}_3$	2-Bromo-1-chloro-1,1-difluoropropane	6.4
$\text{CHBr}_2\text{F}$	Dibromofluoromethane	6.4
$\text{CBrF}_2\text{CH}_2\text{Br}$	1,2-Dibromo-1,1-difluoroethane	6.8
$\text{CF}_3\text{CH}_2\text{Br}$	2-Bromo-1,1,1-trifluoroethane	6.8
$\text{C}_6\text{F}_{11}\text{C}_2\text{F}_5$	Perfluoro(ethylcyclohexane)	6.8
$1,3\text{-C}_6\text{F}_{10}(\text{CF}_3)_2$	Perfluoro(1,3-dimethylcyclohexane)	6.8
$1,4\text{-C}_6\text{F}_{10}(\text{CF}_3)_2$	Perfluoro(1,4-dimethylcyclohexane)	6.8
$\text{CF}_3\text{I}$	Trifluoroiodomethane	6.8
$\text{CH}_2\text{BrCH}_2\text{Cl}$	1-Bromo-2-chloroethane	7.2
$\text{CClF}_2\text{CH}_2\text{Br}$	2-Bromo-1-chloro-1,1-difluoroethane	7.2

Table I (Continued)

<u>Compound Formula</u>	<u>Compound Name</u>	<u>Peak Percentage</u>
$C_6F_{11}CF_3$	Perfluoro(methylcyclohexane)	7.5
$C_7F_{16}$	Perfluoroheptane	7.5
$CH_2BrCl$	Bromochloromethane	7.6
$CHBrF_2$	Bromodifluoromethane	8.4
$CClF_2CCl_2F$	1,1,2-trichlorotrifluoroethane	9.0
$CBrClF_2$	Bromochlorodifluoromethane	9.3
HBr	Hydrogen bromide	9.3
$CH_3Br$	Methyl bromide	9.7
$CF_2=CHBr$	2,2-Difluorovinyl bromide	9.7
$C_4F_{10}$	Perfluorobutane	9.8
$SiCl_4$	Silicon tetrachloride	9.9
$CBrF_2CBrClF$	1,2-Dibromo-2-chloro-1,1,2-trifluoroethane	10.8
$CClF_2CClF_2$	1,2-dichlorotetrafluoroethane	10.8
$CCl_4$	Carbon tetrachloride	11.5
$CF_3CHClCH_3$	2-chloro-1,1,1-trifluoropropane	12.0
$CF_3CH_2CH_2Cl$	3-chloro-1,1,1-trifluoropropane	12.2
$CClF_3$	Chlorotrifluoromethane	12.3
$CF_3CF_3$	Hexafluoroethane	13.4
$CCl_2F_2$	Dichlorodifluoromethane	14.9
$CHCl_3$	Chloroform	17.5
$CHF_3$	Trifluoromethane	17.8
$CHClF_2$	Chlorodifluoromethane	17.9
$C_4F_8$	Octafluorocyclobutane	18.1
$SF_6$	Sulfur hexafluoride	20.5
$BF_3$	Boron trifluoride	20.5



Table I (Continued)

<u>Compound Formula</u>	<u>Compound Name</u>	<u>Peak Percentage</u>
PCl <sub>3</sub>	Phosphorus trichloride	22.5
HCl	Hydrogen Chloride	25.5
CF <sub>4</sub>	Carbon tetrafluoride	26
CO <sub>2</sub>	Carbon dioxide	29.5
H <sub>2</sub> O	Water	>8*
(C <sub>2</sub> F <sub>5</sub> ) <sub>2</sub> NC <sub>3</sub> F <sub>7</sub>	Heptafluoro(N,N-diethylpropylamine)	>8.5
CH <sub>2</sub> Cl <sub>2</sub>	Dichloromethane	>11

\* Concentration limited to vapor pressure of liquid water. Other data indicate that water vapor is less effective than CO<sub>2</sub> as an inhibitor.

Table II

Summary of additives tested in Reference 11. Volume percent refers to amount needed to reduce burning velocity of stoichiometric n-hexane-air burner flame by 30%. Compounds marked with an asterisk were not reported in Reference 11 but were listed in prepublication abstract.

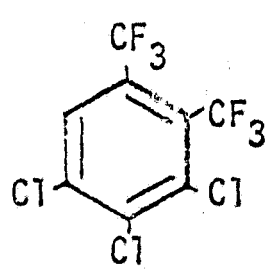
<u>Additive</u>	<u>Volume %</u>	<u>Additive</u>	<u>Volume %</u>
N <sub>2</sub>	8	SnCl <sub>4</sub>	0.19
CO <sub>2</sub>	6.8	TiCl <sub>4</sub>	0.19
n-C <sub>6</sub> H <sub>14</sub>	1.05	SiCl <sub>4</sub>	0.56
Cl <sub>2</sub>	3.3	SiHCl <sub>3</sub>	2.9
Br <sub>2</sub>	0.7	*SO <sub>2</sub> Cl <sub>2</sub>	1.36
CCl <sub>4</sub>	1.38	*SOCl <sub>2</sub>	1.80
CHCl <sub>3</sub>	1.87	*S <sub>2</sub> Cl <sub>2</sub>	1.05
BBr <sub>3</sub>	0.18	Si(CH <sub>3</sub> ) <sub>4</sub>	1.5
PCl <sub>3</sub>	0.15	Fe(CO) <sub>5</sub>	0.017
*POCl <sub>3</sub>	0.19	Pb(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub>	0.015
PSCl <sub>3</sub>	0.13	CrO <sub>2</sub> Cl <sub>2</sub>	<0.024
PBr <sub>3</sub>	0.15		
PSBr <sub>3</sub>	0.15		
(CH <sub>3</sub> ) <sub>3</sub> PO <sub>4</sub>	0.26		
*(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> PO <sub>4</sub>	0.27		
*AsCl <sub>3</sub>	0.39		
*SbCl <sub>3</sub>	0.22		

Table III

Compounds investigated in Reference 56 for suitability as fire extinguishants for flight vehicles. First 10 candidates were found to meet requirements of thermal stability, toxicity, volatility, etc., and are listed in order of decreasing extinguishing strengths when tested on n-heptane-air flames. First six exhibit approximately the same extinguishing effectiveness as chlorobromomethane on a weight basis; last four are about one-half as effective as CB. Remaining twenty-four are listed with the reason for rejection.

<u>Compound Formula</u>	<u>Compound Name</u>
$CF_3CBrClH$	1-Bromo-1-chloro-2,2,2-trichloroethane
$CFC1_2CHCl_2$	1,1,2,2-tetrachloro-1-fluoroethane
$CF_2BrCFC1CF_2CFC1H$	1-Bromo-2,4-dichloro-1,1,2,3,3,4-hexafluorobutane
$H(CF_2)_2CG_2Br$	1-Bromo-2,2,3,3,-tetrafluoropropane
$CF_2BrCFBrH$	1,2-Dibromo-1,1,2-trifluoroethane
$CF_2BrCFBrCl$	1,2-Dibromo-1-chlorotrifluoroethane
$CCl_3CF_2CFC1_2$	1,1,1,3,3-Pentachloro-trifluoropropane
$H(CF_2)_4CH_2Br$	1-Bromo-2,2,3,3,4,4,5,5-octafluoropentane
$H(CF_2)_2CH_2Cl$	1-Chloro-2,2,3,3-tetrafluoropropane
$H(CF_2)_4CH_2Cl$	1-Chloro-2,2,3,3,4,4,5,5-octafluoropentane
<u>Compound</u>	<u>Reason for Rejection</u>
$BrCH_2CO_2CH_2CF_3$	Poor thermal stability
$BrCH_2CO_2CH_2CF_2CF_2H$	Poor thermal stability
$H(CF_2)_6CH_2Br$	Poor low temperature properties
$BrCF_2CFC1CHClCH_2Cl$	Poor thermal stability
$CH_3CHBrCO_2CH_2CF_3$	Poor thermal stability

Table III (Continued)

<u>Compound</u>	<u>Reason for Rejection</u>
$\text{CF}_3\text{CO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$	Poor thermal stability and poor low temperature properties
$\text{CF}_3\text{CF}_2\text{CF}_2\text{CCl}_3$	Poor inhibitor
$\text{CF}_3\text{CF}_2\text{CFCICH}_2\text{Cl}$	Poor thermal stability
$\text{CF}_3(\text{CF}_2)_5\text{CHF}_2$	Poor inhibitor
$(\text{CF}_3(\text{CF}_2)_3)_3\text{N}$	Poor inhibitor
$\text{CF}_2\text{BrCFCICH}_2\text{CH}_2\text{Br}$	Poor thermal stability
	Poor thermal stability
$\text{CF}_2\text{ClCFCICF}_3$	Too high vapor pressure at 500°F
$\text{CFCIBrCFBrCFCICFCI}_2$	Poor thermal stability
$\text{H}(\text{CF}_2)_8\text{CH}_2\text{Cl}$	Solid
$\text{CF}_2\text{BrCF}_2\text{Br}$	Poor thermal stability
$\text{CF}_2\text{BrCFCIH}$	Poor thermal stability
$\text{CFCI}_2\text{CFCI}-\text{CF}=\text{CFCI}_2$	Poor low temperature properties
$\text{CCl}_3\text{CF}_2\text{CFCIBr}$	Poor low temperature properties
Vinyl Bromide Telomer	Poor thermal stability
$\text{CHBrCl}_2$	Poor thermal stability
$(\text{HCF}_2\text{CF}_2\text{CH}_2\text{O})_3\text{P}$	Poor low temperature properties