NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE 3565

CHEMICAL ACTION OF HALOGENATED AGENTS IN FIRE EXTINGUISHING

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Washington
September 1955

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SUMMARY

The action of halogenated agents in preventing flame propagation in fuel-air mixtures in laboratory tests is discussed in terms of a possible chemical mechanism. The mechanism chosen is that of chain-breaking reactions between agent and active particles (hydrogen and oxygen atoms and hydroxyl radicals).

Data from the literature on the flammability peaks of n-heptane-agent-air mixtures are treated. Ratings of agent effectiveness in terms of the fuel equivalent of the agent, based on both fuel and agent concentrations at the peak, are proposed as preferable to ratings in terms of agent concentration alone. These fuel-equivalent ratings are roughly correlated by reactivities assigned to halogen and hydrogen atoms in the agent molecules. It is concluded that the presence of hydrogen in an agent need not reduce its fire-fighting ability, provided there is enough halogen to make the agent nonflammable.

A method is presented for estimating from quenching-distance data a rate constant for the reaction of agent with active particles. A quantitative result is obtained for methyl bromide. This rate constant predicts the observed peak concentration of methyl bromide quite well. However, more data are needed to prove the validity of the method.

The assumption that halogenated agents act mainly by chain-breaking reactions with active particles is consistent with the experimental facts and should help guide the selection of agents for further tests.

INTRODUCTION

The development of effective fire-fighting methods is an important problem in aircraft operations. At the heart of the problem is the need for potent extinguishing agents. In addition to potency, the agents must have properties that make them suitable for use in aircraft environments; for example, the corrosiveness, freezing point, toxicity, and electrical conductivity must be considered.

An extinguishing agent may put out a fire by one or more of the following mechanisms:

(1) Cooling action

(2) Blanketing action (dilution of oxygen around fire)

(3) Mechanical action (cutting fire away from source of combustible)

(4) Chemical action

The commonly used agents, water and carbon dioxide, seem to operate by a combination of the first three modes of action. However, Fryburg (ref. 1) has reviewed the literature pertinent to fire-extinguishing agents, and his analysis emphasizes the importance of chemical action. He concludes that gains may be made by seeking agents that interfere chemically with the combustion reactions, and focuses attention on halogen-containing compounds. More specifically, some of the halogenated hydrocarbons combine chemical effectiveness with physical properties suitable for aircraft use.

Although the case for the existence of chemical action in fire fighting is made in reference 1, it is worthwhile to report the essential arguments here. Studies of the concentration limit of flammability for fuels mixed with oxygen and inert gas (e.g., fuel-air mixtures) show that, for a given fuel, flame cannot propagate unless a fairly definite minimum flame temperature is attained (ref. 2). In other words, the limit occurs at a concentration of fuel that will release just enough heat of combustion to raise the products to the minimum flame temperature. Then, if one tries to prevent flame propagation in any mixture of fuel and air by addition of more inert gas, a gas of high heat capacity would be expected to be more effective than one of low heat capacity. This expectation is confirmed by experiment. For example, reference 3 gives the following order of effectiveness for prevention of flame propagation in methane-air mixtures: carbon dioxide > nitrogen > argon, which is the same as the order of the heat capacities. Halogenated agents, on the other hand, show no such correlation between heat capacity and extinctive ability; the action is not due simply to cooling (ref. 4, p. 115). Furthermore, the amount of halogenated agent required to prevent flame propagation is very much less than the amount of inert gases required (ref. 5). Inasmuch as mechanical action cannot be a factor in the flammability tests, and the diluting action is no more effective than that of the same volume of inert gas, reference 1 concludes that halogenated compounds are good extinguishing agents because of chemical action.

Although the importance of the physical fire-fighting mechanisms should not be ignored, it seems most logical to search for chemically effective agents by means of a test that minimizes the influence of physical factors. Reference 1 points out that flammability-limit studies offer a method of rating chemical action quantitatively. The most suitable test appears to be a determination of the flammability peak. The concentration limits of flammability of homogeneous mixtures of fuel, air, and extinguishing agent are determined, and the smallest amount of agent that will prevent flame propagation in any fuel-air mixture is found; this is called the flammability peak. The smaller the concentration of agent at the peak, the more effective it is. The flammability determinations are carried out by essentially the standard method described in reference 3.

In recent years many halogenated hydrocarbons have been tested for fire-extinguishing potential (see, e.g., refs. 6 to 8). In this way, some highly effective agents have been found. For example, 4.2-percent-by-volume dibromodifluoromethane will prevent flame propagation in all n-heptane-air mixtures, whereas 29.5 percent of the relatively inert carbon dioxide is required (ref. 6, from work by the Purdue Research Foundation). Furthermore, it has been found that there is some correlation between the order of effectiveness of various agents as rated by flammability peaks and the order indicated by practical application tests to standard fires (ref. 6). The work is thus quite well advanced.

However, it is desirable to understand something of the chemistry involved in extinction of a fire by halogenated agents. Such knowledge would aid in selection of agents for test and would help decide the important question of whether still more effective agents remain to be found.

Reference 1 speculates that the chemical action of halogenated agents consists in reaction with and removal of hydrogen atoms. It is the purpose of the present report to interpret flammability-peak data in terms of such a mechanism, but extended to include oxygen atoms and hydroxyl radicals that are also believed to be important in flame propagation. A method of estimating the rate constant for the reaction between active particles and agent molecules is described and illustrated for the case of methyl bromide in propane-air mixtures. No real proof can be advanced for the conclusions derived from this interpretation, but it is presented as a useful basis for discussion and further experimental work.

SYMBOLS

A	fraction of total molecules present in gas phase that must react if flame is to continue to propagate
b	average chain-branching coefficient, sec^{-1}
$c_{a,t}$	agent concentration at flammability peak with respect to total mixture of fuel, air, and agent, percent by volume
c_f	fuel concentration at flammability peak with respect to fuel and air only, percent by volume

$c_{f,r}$	rich-limit fuel concentration in air, percent by volume
$c_{f,t}$	fuel concentration at flammability peak with respect to total mixture of fuel, air, and agent, percent by volume
D_i^o	diffusion coefficient for active particles of one kind into unburned gas at atmospheric pressure and initial mixture temperature, cm^2/sec
D_H^o, D_O^o, D_{OH}^o	diffusion coefficients for H, O, and OH, respectively, into unburned gas at atmospheric pressure and initial mixture temperature, cm^2/sec
d	width of rectangular slot, cm
E	activation energy, cal/mole
Δf	amount of fuel that must be added to fuel-air mixture of concentration c_f to produce rich-limit mixture, moles
g	average chain-breaking coefficient, sec^{-1}
k_a	average specific rate constant for reaction of H, O, and OH with agent molecules, cm^3/molecule/sec
k_f	average specific rate constant for reaction of H, O, and OH with fuel molecules, cm^3/molecule/sec
N_a	number of agent molecules per unit volume, number/cm^3
$N_a(T_R)$	number of agent molecules per unit volume in unburned mixture at reaction temperature, number/cm^3
N_f	number of fuel molecules per unit volume, number/cm^3
$N_f(T_R)$	number of fuel molecules per unit volume in unburned mixture at reaction temperature, number/cm^3
n	power expressing temperature dependence of diffusion coefficient, $D \propto T^n$
P	total pressure of mixture, atm
p_i	partial pressure of active particles of one kind, atm

$p_{i,eq}$	equilibrium adiabatic partial pressure of active particles of one kind, atm
R	universal gas constant, cal/(mole)(°C)
T_F	equilibrium adiabatic flame temperature, °K
T_R	mean reaction temperature, $0.7T_F$, °K
T_0	initial mixture temperature, °K
w	rate of reaction
ε	fraction of total number of active particles striking walls that are destroyed
η_a	fuel equivalent of agent

EXTINGUISHING ACTION OF HALOGENATED AGENTS

Flammability Peaks of Halogenated Agents

Although most halogenated hydrocarbon agents are a good deal more effective than a relatively inert gas such as carbon dioxide, very wide variations in flammability peaks are found; figure 1 shows typical examples from reference 9. Flammability peaks for 54 halogenated hydrocarbon agents as well as data for ten compounds not based on hydrocarbon molecules are listed in reference 6. The fuel used was n-heptane, and the tests were run in the usual flammability-limit apparatus described in reference 3. However, it was convenient to work at pressures from 300 to 500 millimeters of mercury, rather than at 1 atmosphere; the results were probably not much different from those that would have been obtained at 1 atmosphere (ref. 10). The percent of agent by volume at the flammability peak ranged from 4.2 (dibromodifluoromethane) to 26 (carbon tetrafluoride). The large body of consistent data from reference 6 will serve as the main basis for discussion in this report. The data for 46 halogenated hydrocarbons for which flammability peaks were obtained are reproduced in table I.

Inasmuch as the effectiveness of an agent is greater the smaller its concentration at the flammability peak, it is noted in reference 6 that the reciprocal of the peak concentration is a direct measure of the extinguishing ability. Inspection of these reciprocals shows that the halogen atoms stand in the following order of effectiveness: iodine > bromine > chlorine > fluorine.

Fuel Equivalent of Agent as Measure of Extinguishing Ability

As already mentioned, previous work has taken the reciprocal of the peak agent concentration as a direct measure of agent effectiveness. Before going on to a discussion of the chemical action of agents, a new method of rating agents will be discussed. This method accounts for both fuel and agent concentrations in the peak mixture.

Table I shows that the concentration of n-heptane at the flammability peak changes with the agent used; it varies from 0.7 percent by volume in the case of 3-chloro-1,1,1-trifluoropropane, to 4.4 percent in the case of dibromodifluoromethane. Now, the fuel itself is an extinguishing agent, as evidenced by the phenomenon of rich flammability limits. For example, consider mixtures of n-heptane and air; the lean and rich limits are 1.10 and 6.70 percent by volume, respectively, as measured by the standard method (ref. 3). In other words, substitution of 5.60 parts of n-heptane vapor for 5.60 parts of air (by volume) in a lean-limit mixture produces a rich-limit mixture. Thus, the fuel itself is an effective extinguishing agent in the closed system used for flammability tests. (However, the same conclusion would not hold true in the case of an open fire, with ready access of oxygen.) Consequently, it does not seem entirely correct to rate agent effectiveness simply in terms of the agent concentration at the flammability peak. The amount of fuel in the peak mixture should be accounted for as well, and the agent concentration should be compared with the amount of fuel that would have to be added in the absence of agent to attain the rich flammability limit. In addition to separating the effects of fuel and of agent in preventing flame propagation, this method also compares the agents to the fuel on which they are tested, rather than to an arbitrary standard such as the peak concentration of a particular agent.

A mixture of 100 moles of fuel, agent, and air, at a volume composition corresponding to the flammability peak, contains $c_{f,t}$ moles of fuel, $c_{a,t}$ moles of agent, and $(100 - c_{f,t} - c_{a,t})$ moles of air. The fuel concentration c_f, with respect to fuel and air only, is

$$c_f = \left[c_{f,t}/(100 - c_{a,t})\right] 100 \text{ percent by volume (or moles per 100 moles)} \qquad (1)$$

This fuel-air mixture of fuel concentration c_f can be made nonflammable by adding $c_{a,t}$ moles of agent or Δf moles of fuel, sufficient to give a rich-limit mixture. The expression for the rich limit is

$$c_{f,r} = \left[\frac{c_f + \Delta f}{c_f + \Delta f + (100 - c_f)}\right] \times 100 \qquad (2)$$

Equation (2) can be solved for Δf:

$$\Delta f = \frac{c_{f,r} - c_f}{1 - \frac{c_{f,r}}{100}} \tag{3}$$

The ratio

$$\eta_a = \frac{\Delta f}{c_{a,t}} \tag{4}$$

thus defines the fuel equivalent of the agent. The higher the value of η_a, the better the agent. Values of η_a have been calculated for the data of reference 6 and are listed in table I. The order of η_a is not the same as the order of $c_{a,t}$. On the basis of η_a values, $CF_3CH_2CH_2Br$ is the best agent tested for preventing flame propagation in flammability tests; in order of increasing agent concentration at the flammability peak, this agent stands tenth.

Chemical Effectiveness of Extinguishing Agents

Flame propagation and extinction. - It has already been pointed out that the effectiveness of a halogenated agent comes from some chemical action. In order to judge what the mode of such action might be, it is necessary to adopt a general scheme for the essential chemical reactions of combustion.

As yet, there is very little information on the kinetics of high-temperature combustion reactions. Direct experimental methods that may finally decide the reaction mechanism are still under development. Meanwhile, combustion reactions must be studied mainly by indirect means. A chemical scheme is assumed, and data on such properties as burning velocity and quenching distance are examined for consistency with the asssumptions.

In recent years, the theory that flame propagation depends on reactions between active particles (atoms and free radicals) and fuel has received considerable attention (refs. 11 and 12) and has proved consistent with a large body of data relating to laminar flames (ref. 13). This theory is based on the fact that active particles are known to exist in flames, and some of these particles are found to be very reactive toward fuel molecules in separate experiments (ref. 14). Reference 12 and many subsequent papers emphasize the importance of hydrogen and oxygen atoms and hydroxyl radicals in starting reaction chains.

The idea that reaction chains started by H, O, and OH are needed for hydrocarbon flame propagation was therefore adopted in the present work. It is an easy extension to consider the case in which the mixture contains a halogenated agent. As the active particles travel about in the reaction zone, some of them will meet agent molecules. If a reaction then occurs that ties up active particles in stable products, without creation of new active particles, the agent acts as a chain-stopper. If there is enough of this chain-stopping action, the agent will extinguish the flame. This model of flame extinction is equivalent to the one suggested by reference 1; however, reference 1 considered the hydrogen atom as the most important active particle. The present model includes oxygen atoms and hydroxyl radicals in view of the later work summarized by reference 13.

Inasmuch as the detailed chemical mechanism of combustion is not known from direct study, this model of extinction cannot be argued on an absolute basis. For example, if the reaction between an active particle and an agent molecule should yield a methyl radical, it is by no means clear that the methyl radical should be a less effective chain initiator than the active particle that disappeared in the reaction. However, it is fruitless to speculate on such complications at this time. In this discussion, only the following two steps will be considered in the chain mechanism:

(1) The rate-controlling reaction between active particles and fuel

(2) The chain-breaking reaction between active particles and agent

Some initial support for the active-particle idea of flame extinction may be obtained from the literature, as pointed out in reference 1. Reference 14 shows that the rate of reaction of hydrogen atoms with singly halogenated methanes decreases in the order iodine > bromine > chlorine > fluorine. As already mentioned, the order of effectiveness of halogen atoms in extinguishing agents is the same.

Reactivity numbers for halogenated agents. - The model described in the preceding section may be carried a bit further, by means of a crude approach, and a rough correlation of the fuel equivalent η_a data of table I obtained. Reactivities were assigned to the various halogen atoms on the basis of the reactions of hydrogen atoms with the singly halogenated methanes. The following data are available from reference 14:

$$H + CH_3F \rightarrow CH_3 + HF \qquad E > 9000 \text{ cal/mole} \tag{5}$$

$$H + CH_3Cl \rightarrow CH_3 + HCl \qquad E = 7000 \text{ to } 9000 \text{ cal/mole} \tag{6}$$

$$H + CH_3Br \rightarrow CH_3 + HBr \qquad E = 3000 \text{ to } 7000 \text{ cal/mole} \tag{7}$$

$$H + CH_3I \rightarrow CH_3 + HI \qquad E < 5000 \text{ cal/mole} \tag{8}$$

Only reactions of hydrogen atoms were considered, because a similar set of data for oxygen atoms and hydroxyl radicals was not available.

Rates of reaction w are exponential functions of the activation energies and the temperature:

$$w \propto e^{-E/RT_R} \tag{9}$$

The following activation energies were chosen for reactions (5) to (8):

Reaction	Activation energy, E, cal/mole
(5)	10,000
(6)	8,000
(7)	5,000
(8)	2,000

The value 2000 cal/mole for reaction (8) was estimated from a plot of E against atomic weight of halogen for the other three reactions.

The mean reaction temperature T_R was taken as

$$T_R = 0.7T_F \tag{10}$$

as in reference 12. For the present purpose, T_F was set equal to the flame temperature calculated for the n-heptane-air mixture of maximum burning velocity, 2208° K (ref. 15); therefore, $T_R \sim 1550^\circ$ K. Table II lists the values of the exponentials computed in this manner, as well as the values relative to the smallest reactivity (for reaction (5)). The latter are relative reactivities and are more convenient to handle.

The relative reactivities were derived from reactions of methyl halides. However, it was assumed that the same reactivity applies to a given kind of halogen atom, regardless of the structure of the molecule in which it appears. The total reactivity of the agent with respect to halogen was thus found by adding the relative reactivities for all the halogen atoms present. These numbers, however, did not correlate the η_a values listed in table I.

Many of the widely-scattered points were for hydrogen-containing agents, and the η_a values tended to be too high. Now, reactions of the following kind are known to occur easily (ref. 14):

$$H + C_2H_6 \rightarrow H_2 + C_2H_5 \qquad E = 6700 \text{ cal/mole} \tag{11}$$

If such a reaction were to occur between a hydrogen atom and a hydrogen-containing agent, the chain carrier (H) would be destroyed and the remaining radical (a halogenated group analogous to C_2H_5 in reaction (11)) might still have an extinguishing effect. In that case, the total agent reactivity should include a reactivity assigned to hydrogen atoms in the agent molecule. Reaction (11) was assumed fairly representative of the reactions that would be experienced by H at the hydrogen sites of agent molecules.

When a reactivity for hydrogen atoms based on $E = 6700$ cal/mole was added to that for the halogen atoms, the rough correlation of the η_a data with total reactivity shown in figure 2(a) was obtained. The solid line in figure 2(a) was drawn by eye; the dashed lines bound the region of ±25-percent deviation in total reactivity. Only eight points lie markedly outside this region.

The correlation of figure 2(a) certainly does not prove the validity of the active-particle approach, but there are several noteworthy points that summarize the findings:

(1) The reactivity numbers correlate the η_a data better than they correlate the peak agent concentrations. This may be seen by comparing figure 2(a) with figure 2(b), in which total reactivity is plotted against reciprocal peak agent concentration. Fifteen points lie outside the region of ±25-percent deviation in total reactivity bounded by the dashed lines.

(2) The reactivity of hydrogen atoms present in the agent had to be added to that of the halogen atoms in order to obtain figure 2.

(3) The best halogen reactivities found by trial and error in reference 6 were

$$F:Cl:Br:I = 1:2:10:16$$

The relative numbers used in this work were somewhat similar (table II):

$$F:Cl:Br:I = 1:1.9:5.1:13.4$$

The main difference is in the bromine reactivity. However, of the 22 bromine-containing agents listed in table I, 15 contain hydrogen. Therefore, inclusion of hydrogen in the total reactivities calculated in the present work presumably accounts for the difference.

(4) Reference 6 used the trial-and-error reactivities to calculate peak agent concentrations. The observed and calculated values of $c_{a,t}$ are compared in figure 2(c). The solid line is the perfect correlation line, and the dashed lines bound the region of ±25-percent deviation in calculated $c_{a,t}$ values. Comparison of figures 2(a) and (c) shows that the correlation developed in the present paper is at least as good as the best empirical correlation.

The procedures adopted in this report thus appear to be useful; and, furthermore, the active-particle idea of flame extinction leads to a suggestion that may be quite important. That is, it appears that effective agents are not necessarily completely halogenated hydrocarbons, and that good agents may contain hydrogen as long as there is enough halogen to make the agent nonflammable. Thus, on the basis of the η_a values of table I, $CF_3CH_2CH_2Br$ is rated as the best agent, followed by CH_2Br_2 and CBr_3F, whereas reference 6 rates CBr_2F_2 and CBr_3F as best on the basis of the amount of agent required to produce a flammability peak.

The value of hydrogen in agents should be an important factor in keeping practical agents both volatile and cheap. Comparison of the amount of halogen in the agents listed as flammable in reference 6 with the amount in nonflammable agents shows that the critical proportion is about 75 percent by weight.

METHODS OF CALCULATING AGENT REACTIVITY FROM EXPERIMENTAL DATA

Basis of Calculations

Very little information is available on the chemical mechanism of combustion reactions, and attempts to explain the chemical action of halogenated agents must start with some assumptions about the key steps in the mechanism. In this work, the assumption is that reaction of active particles (specifically, H, O, and OH) with fuel and agent governs flame propagation in hydrocarbon-agent-air mixtures. This assumption led to the set of reactivities for halogen and hydrogen atoms in agent molecules that has been discussed. However, the reactivities had to be obtained in an unrealistic manner, and the correlation of η_a data to which they lead (fig. 2(a)) is not very satisfying.

Granted a similar assumption about the mechanism of flame propagation, it is possible to derive better measures of agent reactivity from suitable experimental data. One approach is described in reference 16, in which the flammability limits of carbon monoxide and of hydrogen in air were measured with various amounts of added methyl bromide. The combustion products were analyzed for water, hydrogen, hydrogen bromide, and so forth; suitable mass balances were generally obtained. These results were used to compute the adiabatic flame temperatures for mixtures near the flammability limits. The flame-propagation theory of Van Tiggeln (ref. 17, p. 419), which pictures flammability limits as being fixed by the relative probabilities of chain-breaking and -branching, was then applied. Activation energies for the two types of reaction were derived, and reference 16 suggests that the actual reactions might be as follows:

$$H + O_2 \rightarrow OH + O \text{ (chain-branching)} \qquad (12)$$

$$H + CH_3Br \rightarrow CH_3 + HBr \text{ (chain-breaking)} \qquad (13)$$

This method, then, yields activation energies for the branching and breaking reactions that are assumed to take place. It may be noted that the chain-breaking reaction is the one suggested in reference 1.

An altogether different approach, which is described in detail in the next section, depends upon the use of quenching-distance data and equations that interpret quenching from the active-particle point of view. Average rate constants for the reaction of H, O, and OH with agent may be computed; from them the amount of agent at the flammability peak may be estimated and compared with experiment to check the calculation.

Description of Method for Calculating Reactivity from Quenching-Distance Data

It has long been known that a flame in a mixture of given temperature, pressure, and composition will not travel through a tube smaller than some minimum size (see, e.g., ref. 5). This minimum size is called the quenching distance, and it may be the diameter of a circular tube or the width of a rectangular one. The numbers, however, are not the same in both cases, so there is a geometry effect.

Reference 18 adopts the point of view that a flame is quenched when a critical proportion of the active particles (H, O, and OH) produced in the flame strike the walls, where they are assumed to be destroyed. Equations are derived that give the quenching distance in terms of a balance between the number of active particles lost by diffusion to the walls and the number that must diffuse into the fresh gas to sustain flame propagation. These equations have been tested with a good deal of success (refs. 18 to 21); the effects of pressure, temperature, geometry of the quenching surface, and mixture composition (lean-to-stoichiometric mixtures only) have been interpreted.

The original equations of reference 18 were developed on the assumptions that the active particles start straight-chain reactions upon fruitful collisions with fuel molecules and that there is no chain-breaking in the gas phase. Reference 21 considers the case in which there is chain-breaking and derives an equation that may be applied to mixtures containing a supposed chain-breaker, for example, a halogenated agent. The following equation was obtained:

$$d^2 = \frac{12\left[A - \dfrac{(1-\varepsilon)0.7}{1 - \dfrac{g-b}{k_f N_f}} \sum_i \dfrac{p_i}{P}\right]\left(\dfrac{T_R}{T_0}\right)^n}{k_f N_f \left[1 + \dfrac{(1-\varepsilon)0.7}{1 - \dfrac{k_f N_f}{g-b}}\right] \sum_i \dfrac{p_i}{D_i^o}\left[1 - \dfrac{Pd^2(g-b)}{10 D_i^o}\left(\dfrac{T_0}{T_R}\right)^n\right]} \tag{14}$$

It should be emphasized at this point that it is not necessary to assume that active particles are lost by diffusion. An equation analogous to equation (14) might be derived based on the idea that heat loss governs flame propagation in tubes, while retaining the notion that reaction of active particles with fuel is essential. Reference 22 treats flame quenching by tube walls in this manner; however, an equation for the case of gas-phase chain-breaking is not derived. Thus, equation (14) is used in the present work because it was already available.

Reference 21 analyzed a large amount of quenching-distance data and concluded that chain-branching may be neglected $(b = 0)$ and that the efficiency of the wall for destruction ε may be set equal to unity for purposes of the theory. With these changes, equation (14) simplifies to

$$d^2 = \frac{12A\left(\dfrac{T_R}{T_0}\right)^n}{k_f N_f\left[\sum_i \dfrac{p_i}{D_i^o} - \dfrac{Pd^2 g}{10}\left(\dfrac{T_0}{T_R}\right)^n \sum_i \dfrac{p_i}{(D_i^o)^2}\right]} \tag{15}$$

Now, the frequency of chain-breaking reactions g is given by

$$g = k_a N_a \tag{16}$$

The quenching distance d for a mixture of hydrocarbon fuel, air, and agent may be measured. If all the other terms in equation (15) were known, it would be possible to solve for g. The number of agent molecules N_a may be computed from the perfect gas law, so k_a could then be obtained by equation (16). The result would be a measure of the reactivity of an extinguishing agent and, therefore, a measure of its value.

Reference 21 correlates quenching-distance data with the use of the following considerations:

(1) The fraction A was set equal to the mole fraction of fuel at the lean flammability limit.

(2) The mean reaction temperature T_R was calculated from equation (10).

(3) The partial pressure of active particles of one kind in the reaction zone p_i was taken as 0.7 of $p_{i,eq}$, the equilibrium adiabatic partial pressure in the flame.

(4) The equilibrium adiabatic quantities T_F and $p_{i,eq}$ were computed by the method of reference 23.

(5) The amount of fuel in the reaction zone N_f was taken as half the amount $N_f(T_R)$ computed by the perfect gas law from fuel concentration and reaction-zone temperature T_R. This allows for the fact that the average fuel concentration in the reaction zone must be less than would be present in fresh gas at the same temperature, owing to reaction.

The same considerations were adopted in the present work. In addition, N_a was set equal to $0.5N_a(T_R)$, in analogy to assumption (5). Finally, the following values of n and D_i^o were used (ref. 21): $n = 2$; $D_H^o = 1.80\ \text{cm}^2/\text{sec}$; $D_O^o = 0.40\ \text{cm}^2/\text{sec}$; and $D_{OH}^o = 0.28\ \text{cm}^2/\text{sec}$. Solving equations (15) and (16) for k_a then yields

$$k_a = \frac{10d^2k_fN_f\sum_i \frac{p_i}{D_i^o} - 120A\left(\frac{T_R}{T_O}\right)^2}{Pd^4k_fN_fN_a\left(\frac{T_O}{T_R}\right)^2\sum_i \frac{p_i}{(D_i^o)^2}} \tag{17}$$

Appropriate data for use in equation (17) are reported in reference 24. The pressure limits of flame propagation for propane-air mixtures containing 0.5-volume-percent methyl bromide were measured in a tube 3.73 centimeters in diameter. These limits are really the pressure-concentration boundary at which the quenching distance is equal to the tube diameter, as shown in reference 18. Equation (17) applies to the case in which the quenching surface is composed of plane-parallel plates; but the circular-tube quenching distances of reference 17 may be reduced to the corresponding parallel-plate separations if multiplied by the empirical factor 0.7 (ref. 18). In other words, the data for a 3.73-centimeter tube are the same as the data for plates separated by 2.61 centimeters. The pressure-limit curve from reference 24 is reproduced in figure 3.

Reference 21, which also dealt with propane as fuel, suggested for k_f the semiempirical value 2.25×10^{-13} cm^3/molecule/sec. The mole fraction of propane at the lean limit in air is 0.0201 (ref. 2). As for T_F and $p_{i,eq}$, these were approximated by the values computed for propane-air mixtures and reported in reference 18, since the mixtures being treated contained only 0.5-volume-percent methyl bromide.

All the data needed for equation (17) are therefore at hand and are listed in table III for four lean-to-stoichiometric mixtures. Average rate constants calculated from equation (17) for the reaction of H, O, and OH with methyl bromide are listed in table III. The values range from 0.31×10^{-14} cm^3/molecule/sec for the leanest mixture to 7.01×10^{-14} cm^3/molecule/sec for the stoichiometric mixture; the average of the four values is 3.45×10^{-14}. If k_f is 2.25×10^{-13} cm^3/molecule/sec, then methyl bromide is on the average only 15 percent as reactive toward active particles as is propane.

Check of Method by Comparison of Predicted and Observed Flammability Peaks for Methyl Bromide

The result of the foregoing calculation may be checked by using it to estimate the amount of methyl bromide at the flammability peak. In the model used in this work, flame can propagate only if the average chain length is equal to or greater than 1. The chain length is reduced both by destruction of active particles at the walls and by collisions with agent molecules in the gas phase. At pressures near 1 atmosphere and for large tubes, the wall effects are small; the equation in reference 21 for the chain length reduces to the following simple form for the conditions of the flammability tests of reference 6 (500-mm-Hg pressure, 5-cm tube):

$$k_a N_a = k_f N_f \tag{18}$$

This equation means that no flame can propagate if the frequency of gas-phase chain-breaking reactions $k_a N_a$ is equal to the frequency of chain-propagating reactions $k_f N_f$; this is a reasonable statement.

Equation (18) may immediately be written in terms of the volume percent of fuel and agent at the flammability peak $c_{f,t}$ and $c_{a,t}$, respectively, and solved for $c_{a,t}$:

$$c_{a,t} = \frac{k_f}{k_a} c_{f,t} \tag{19}$$

No data were found that gave $c_{f,t}$ for propane-air - methyl bromide mixtures. However, k_f is the same for a large number of saturated hydrocarbons (ref. 15), and k_a should not depend on the fuel used in its determination. Therefore, equation (19) ought to apply to n-heptane, for which both $c_{f,t}$ and $c_{a,t}$ are available from reference 6. Using this data, the estimated methyl bromide concentration at the flammability peak for n-heptane is 3787

$$c_{a,t} = \frac{2.25\times10^{-13}}{3.45\times10^{-14}} 1.4 = 9.1 \text{ volume percent}$$

Reference 6 gives 9.7 percent; the prediction is thus quite good.

DISCUSSION

This report has discussed a mode of agent action based on chain-breaking collisions between agent and active particles. A new method of rating agents in terms of fuel equivalent was proposed; total reactivities that account for both halogen and hydrogen in agent molecules were then derived and used to correlate the fuel-equivalent data. The reactivities were obtained at the expense of much oversimplification. Nevertheless, the chain-breaking model of agent action puts the results of flammability-peak determinations into a fairly consistent pattern; the correlation shown in figure 2(a) between fuel equivalent of agent and estimated reactivity toward active particles may be useful in choosing agents for field tests.

In order to obtain a better and more direct measure of agent reactivity, a method of calculating rate constants for agent-active particle reactions from quenching-distance data was described. The single quantitative result was the average rate constant calculated for reaction of active particles with methyl bromide. This constant closely predicts the observed methyl bromide concentration at the flammability peak for n-heptane, even though it was obtained from entirely unrelated data. However, the agreement may be fortuitous. Quenching-distance data for other agents would have to be measured and the rate constants calculated and correlated with η_a before this reservation could be removed. A further check would be to obtain data for various fuels, but with the same agent; if the model is correct, k_a should not be affected by the fuel.

There is another question that seems beyond the reach of the present simple treatment. The amount of fuel at the flammability peak varies with the agent used, and the peak mixture is sometimes fuel-lean but more often fuel-rich. From the active-particle picture, one would expect that the flammability peak should fall at a fuel concentration corresponding to the maximum production of active particles, that is, at the mixture with the flame most difficult to put out. Perhaps it is most often a rich mixture, because the agent is a diluent and heat sink as well as a chemical participant. Similar behavior is found in studies of burning velocity; the highest burning velocity occurs in progressively richer mixtures as the proportion of nitrogen in the oxidant is increased (ref. 25).

On the other hand, the explanation may have to do with the ignition properties of the fuel. The n-heptane-air mixture most easily ignited by electric sparks is quite rich, about 1.8 times stoichiometric or 3.4 volume percent (ref. 5, p. 413); this is in contrast to the n-heptane-air mixture of greatest burning velocity, which is just rich of stoichiometric (ref. 15). It may be noted that the average n-heptane concentration with respect to fuel and air only c_f (table I) for the 46 agents of reference 6 is 3.1 volume percent, not very different from the most easily ignited mixture.

CONCLUSIONS

The following conclusions were reached in this work:

1. Ratings of agent effectiveness in terms of the fuel equivalent of the agent, based on both the fuel and agent concentrations at the flammability peak, are roughly correlated by reactivities toward active particles assigned to halogen and hydrogen atoms in the agent molecules.

2. The presence of hydrogen in an agent does not necessarily reduce its fire-fighting ability and may actually enhance it, provided there is enough halogen to make the agent nonflammable.

3. A rate constant for the reaction of agent with active particles (hydrogen and oxygen atoms and hydroxyl radicals) may be estimated from quenching-distance data. The result for the only case studied (methyl bromide) is reasonable and predicts the observed peak agent concentration quite well.

4. The assumption that agents act by chain-breaking reaction with active particles is consistent with the experimental facts and should help in the choice of agents for further evaluation. However, a good deal more work is needed to put this theory of the chemical mechanism of fire extinction on a sound basis.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, July 18, 1955

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TABLE I. - FLAMMABILITY PEAKS OF n-HEPTANE-AGENT-AIR MIXTURES

(REF. 6)

Agent	Peak fuel concentration, $c_{f,t}$, percent by volume	Peak agent concentration, $c_{a,t}$, percent by volume	Peak fuel concentration (fuel and air only), c_f, percent by volume	Fuel equivalent of agent, η_a
CBr_2F_2	4.4	4.2	4.6	0.55
CBr_3F	3.0	4.3	3.1	.91
$CBrF_2CH_2Br$	3.4	4.3	3.6	.77
$CBrF_2CBrClF$	3.5	4.6	3.7	.70
$CF_3CHBrCH_3$	3.5	4.9	3.7	.65
$CBrF_2CBrF_2$	3.3	4.9	3.5	.69
CF_2ICF_2I	3.5	5.0	3.7	.64
CH_2Br_2	2.1	5.2	2.2	.92
CF_3CF_2I	3.0	5.3	3.2	.70
$CF_3CH_2CH_2Br$	1.5	5.4	1.6	1.02
CH_3CH_2I	2.3	5.6	2.4	.82
CF_3CBrF_2	4.0	6.1	4.3	.43
CH_3I	2.1	6.1	2.2	.79
$CBrF_3$	3.0	6.1	3.2	.61
CH_3CH_2Br	2.3	6.2	2.5	.73
$CH_2BrCF_2CH_3$	2.3	6.3	2.5	.71
$CClF_2CHBrCH_3$	1.5	6.4	1.6	.86
$CHBr_2F$	3.4	6.4	3.6	.52
CF_3CH_2Br	3.4	6.8	3.7	.47
$C_6F_{11}C_2F_5$	3.4	6.8	3.7	.47
1,3-$C_6F_{10}(CF_3)_2$	3.4	6.8	3.7	.47
CF_3I	2.5	6.8	2.7	.63
1,4-$C_6F_{10}(CF_3)_2$	3.4	6.8	3.7	.47
CH_2BrCH_2Cl	1.7	7.2	1.8	.72
$CClF_2CH_2Br$	3.0	7.2	3.2	.51

TABLE I. - Concluded. FLAMMABILITY PEAKS OF n-HEPTANE-AGENT-AIR MIXTURES (REF. 6)

Agent	Peak fuel concentration, $c_{f,t}$, percent by volume	Peak agent concentration, $c_{a,t}$, percent by volume	Peak fuel concentration (fuel and air only), c_f, percent by volume	Fuel equivalent of agent, η_a
$C_6F_{11}CF_3$	3.0	7.5	3.2	0.49
C_7F_{16}	3.0	7.5	3.2	.49
CH_2BrCl	2.2	7.6	2.4	.61
$CHBrF_2$	4.0	8.4	4.4	.30
$CClF_2CCl_2F$	4.0	9.0	4.4	.28
$CBrClF_2$	3.0	9.3	3.3	.39
CH_3Br	1.4	9.7	1.6	.57
$CF_2=CHBr$	2.6	9.7	2.9	.42
C_4F_{10}	3.4	9.8	3.8	.32
$CClF_2CClF_2$	3.0	10.8	3.4	.38
CCl_4	3.2	11.5	3.6	.29
$CF_3CHClCH_3$	1.0	12.0	1.1	.50
$CF_3CH_2CH_2Cl$	.7	12.2	.8	.52
$CClF_3$	3.3	12.3	3.8	.25
CF_3CF_3	3.0	13.4	3.5	.25
CCl_2F_2	3.9	14.9	4.6	.15
$CHCl_3$	3.6	17.5	4.4	.14
CHF_3	2.5	17.8	3.0	.22
$CHClF_2$	2.3	17.9	2.8	.24
C_4F_8	2.3	18.1	2.8	.23
CF_4	1.8	26.0	2.4	.18

TABLE II. - REACTIVITIES OF HALOGEN AND HYDROGEN ATOMS IN AGENT MOLECULES

Reaction	Activation energy, E, cal/mole	e^{-E/RT_R} (a)	Relative reactivity
$H+CH_3F$	10,000	0.039	1.0
$H+CH_3Cl$	8,000	.075	1.9
$H+CH_3Br$	5,000	.198	5.1
$H+CH_3I$	2,000	.522	13.4
$H+C_2H_6$	6,700	.114	2.9

[a] T_R assumed constant, 1550° K.

TABLE III. - CALCULATED AVERAGE RATE CONSTANTS FOR REACTION BETWEEN ACTIVE PARTICLES AND METHYL BROMIDE

Propane in air, volume percent	Pressure limit, mm Hg (a)	Flame temperature, °K (b)	Partial pressure of H, atm (b)	Partial pressure of O, atm (b)	Partial pressure of OH, atm (b)	Calculated average rate constant, k_a, cm^3/molecule/sec
2.50	210	1718	0.04×10^{-5}	0.87×10^{-5}	9.75×10^{-5}	0.31×10^{-14}
3.00	100	1932	.52	3.61	19.9	1.79
3.50	68	2094	3.29	6.93	29.8	4.70
4.03	56	2184	10.2	7.1	31.5	7.01

[a] Ref. 24 and fig. 3.

[b] Ref. 18.

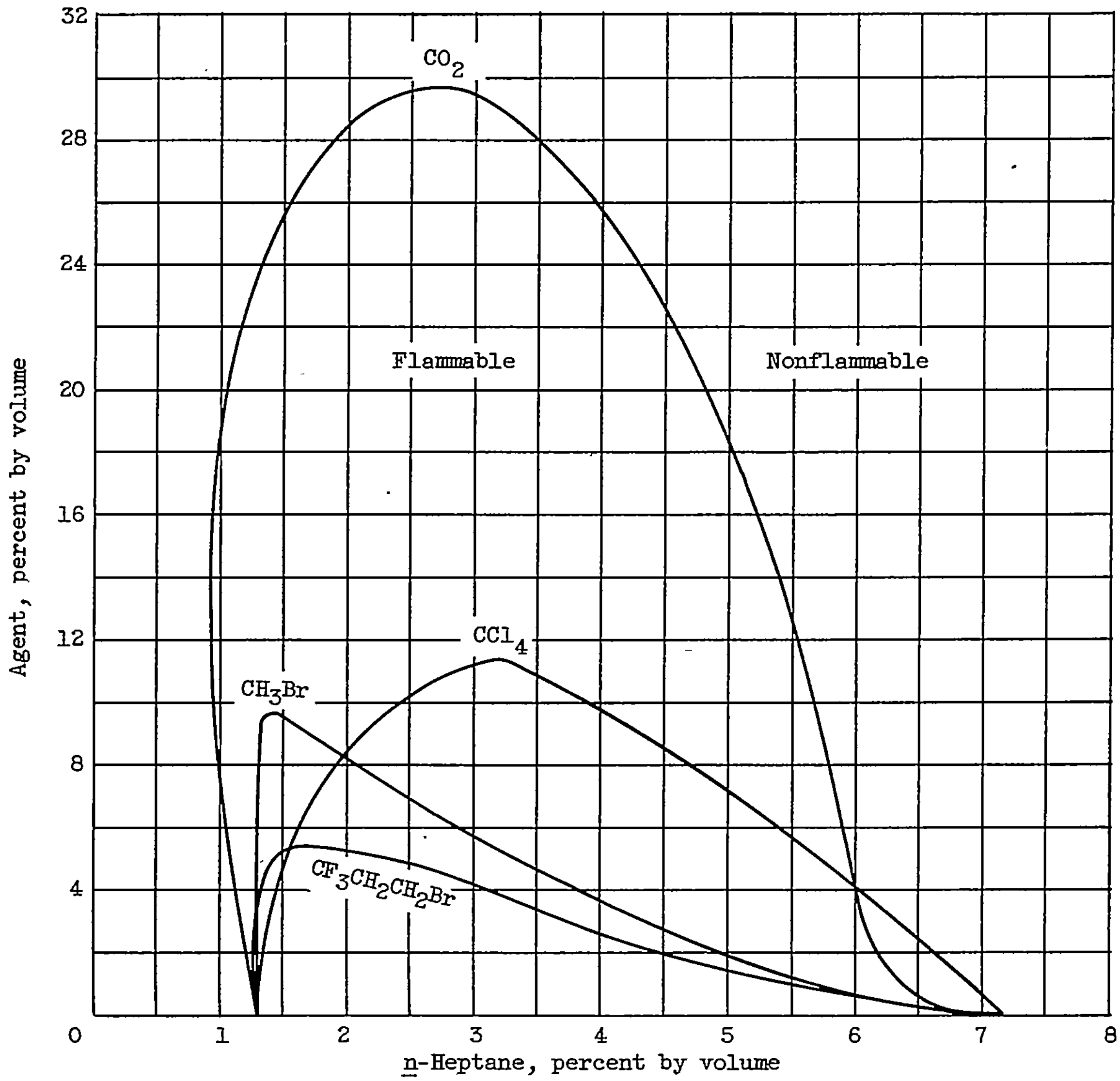
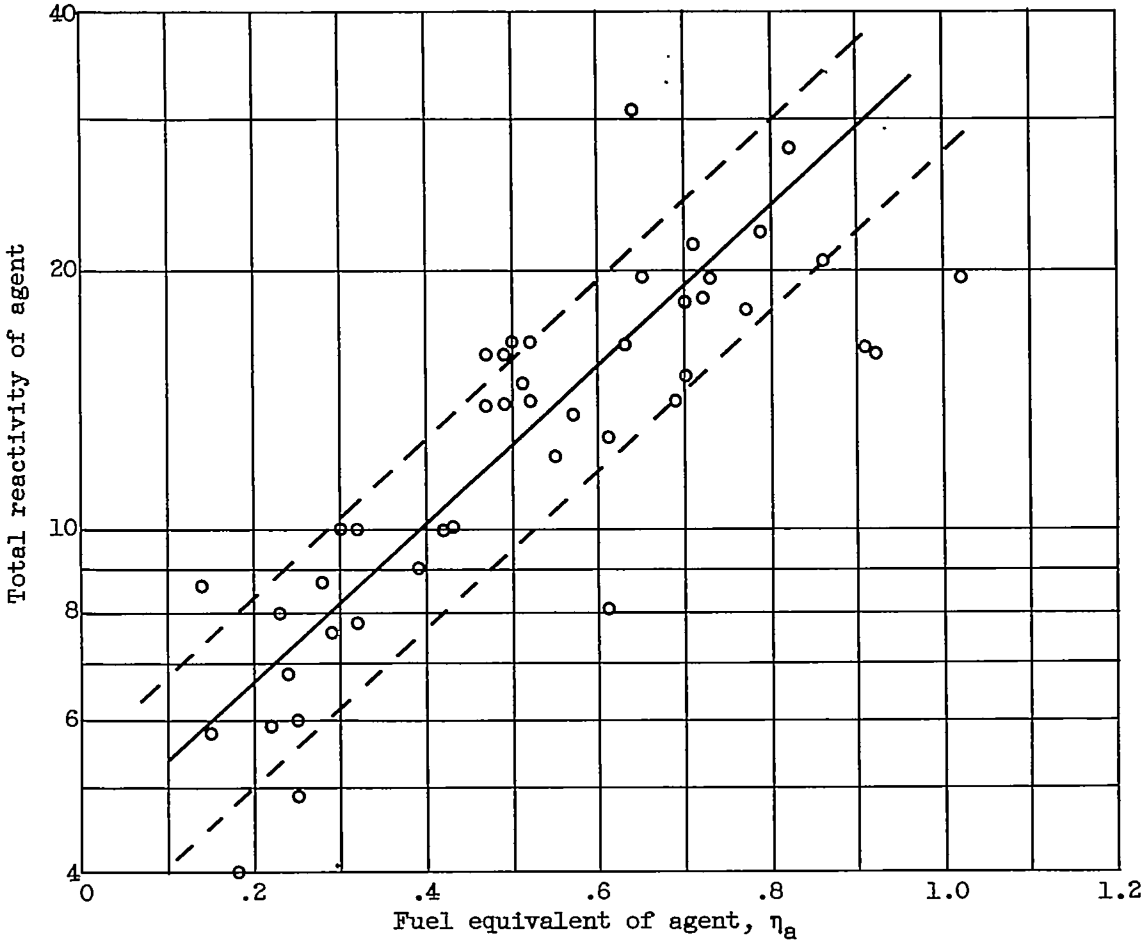
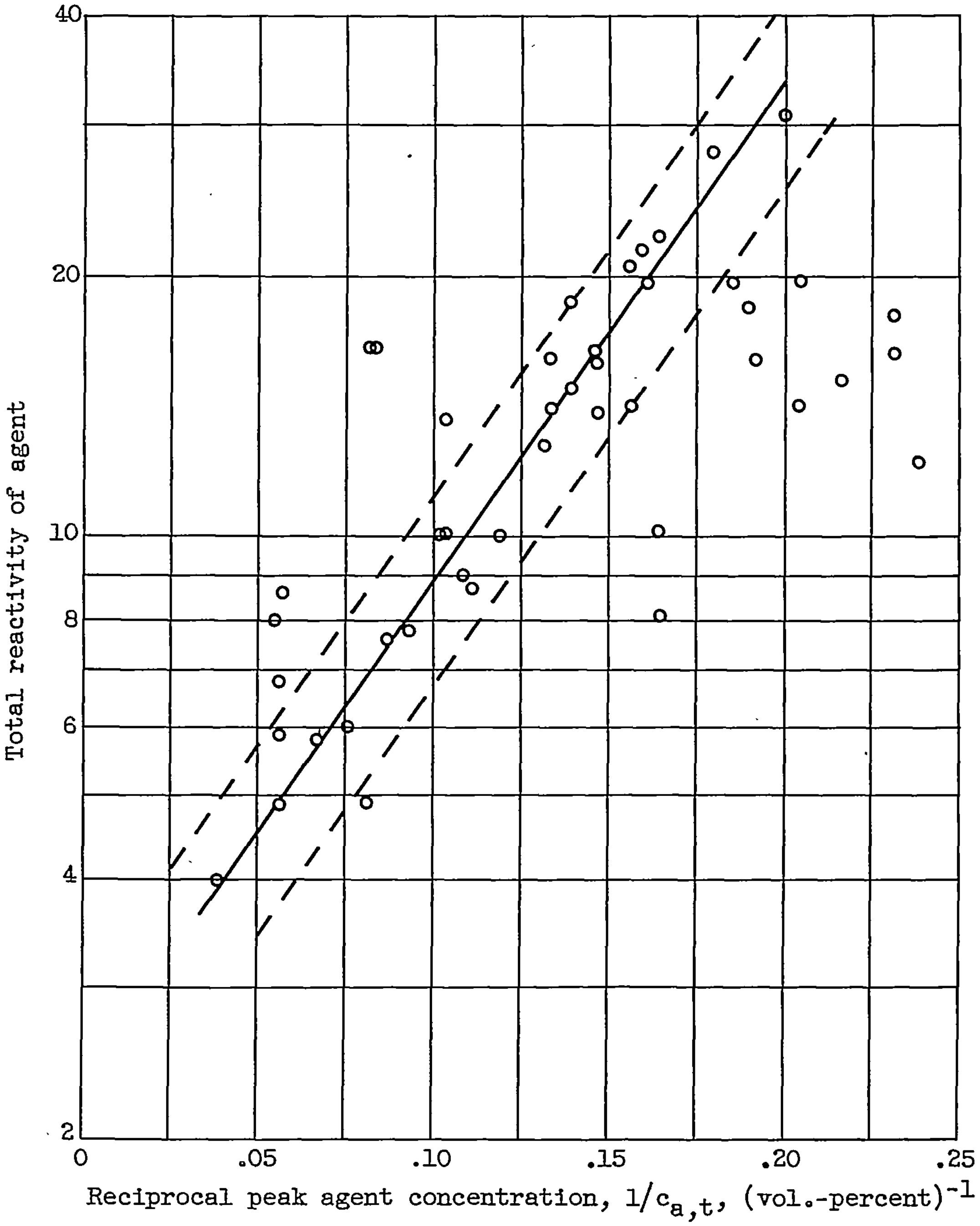


Figure 1. - Flammability limits and flammability peaks of typical n-heptane-agent-air mixtures (ref. 9).



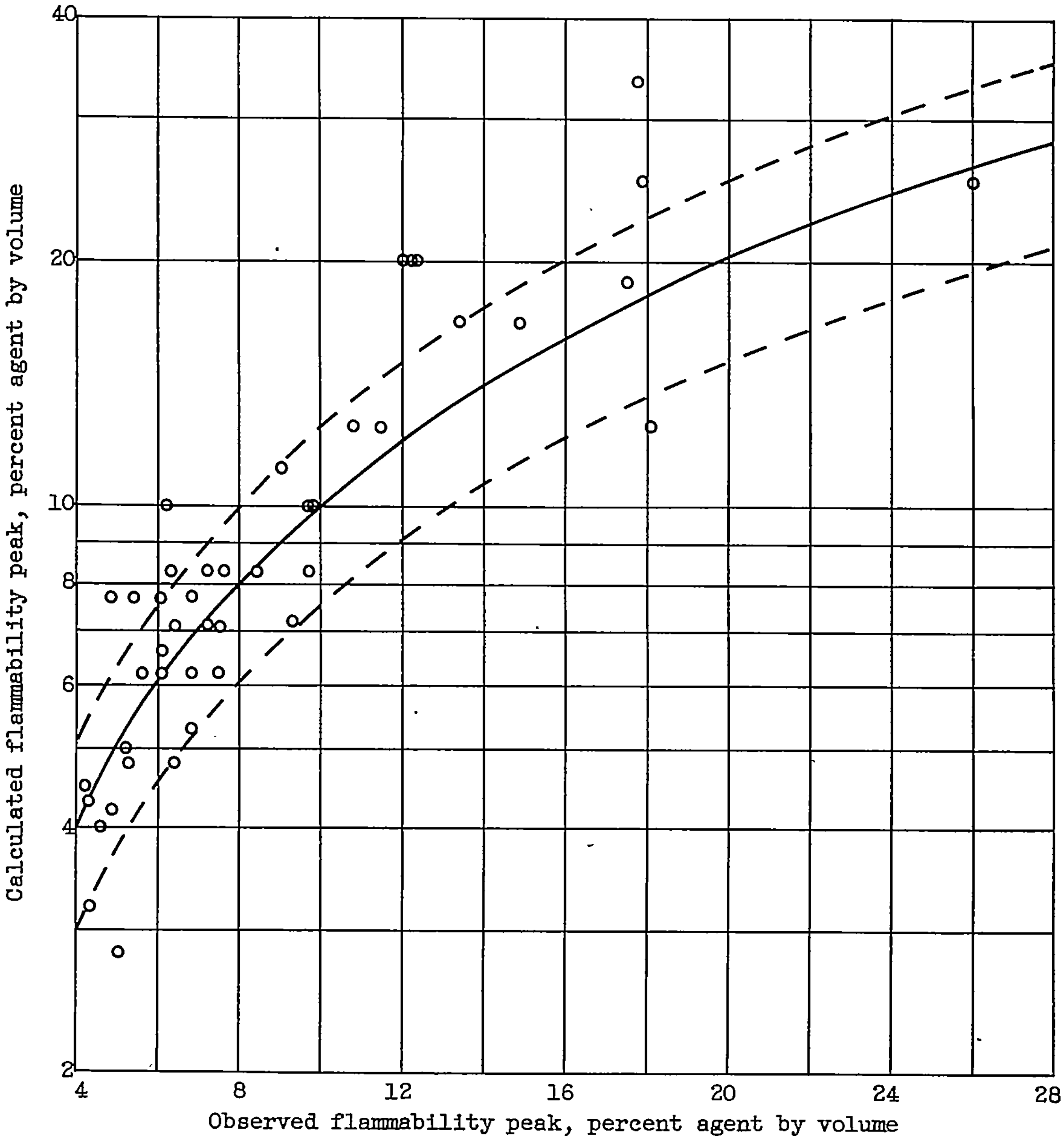
(a) Correlation between fuel equivalent and total reactivity of agent.

Figure 2. - Comparison of observed and calculated measures of agent effectiveness.



(b) Correlation between reciprocal peak agent concentration and total reactivity of agent.

Figure 2. - Continued. Comparison of observed and calculated measures of agent effectiveness.



(c) Comparison of observed peak agent concentrations with those calculated from empirical trial-and-error reactivities for halogen atoms (ref. 6).

Figure 2. - Concluded. Comparison of observed and calculated measures of agent effectiveness.

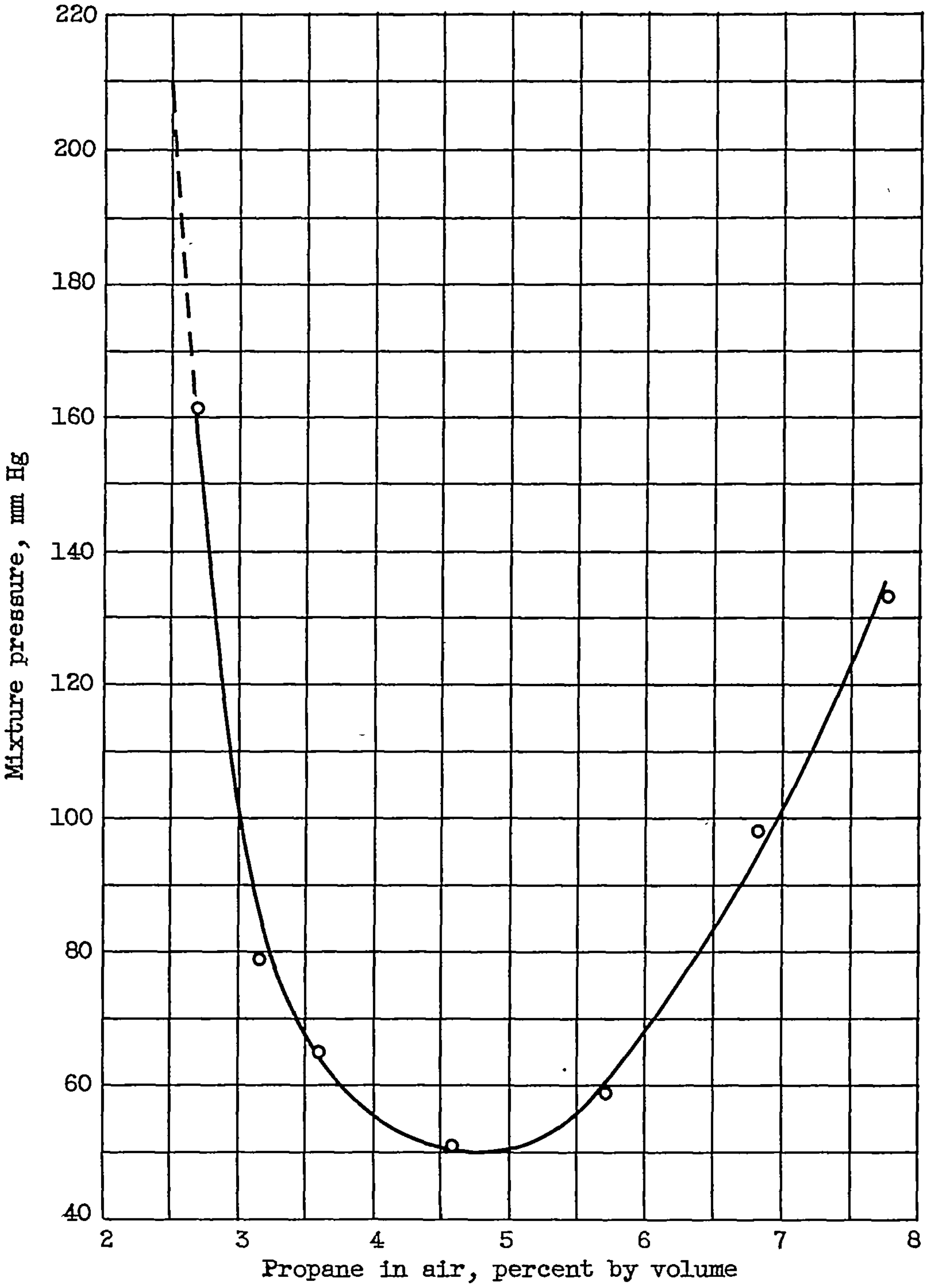


Figure 3. - Pressure limits of flame propagation for propane-agent-air mixtures containing 0.5 volume-percent methyl bromide (ref. 24).