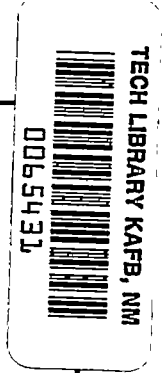


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NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE 2102

REVIEW OF LITERATURE PERTINENT TO FIRE-EXTINGUISHING
AGENTS AND TO BASIC MECHANISMS
INVOLVED IN THEIR ACTION

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REVIEW OF LITERATURE PERTINENT TO FIRE-EXTINGUISHING AGENTS
AND TO BASIC MECHANISMS INVOLVED IN THEIR ACTION

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SUMMARY

Literature relating to fire-extinguishing agents was reviewed in order to ascertain the extent of present knowledge and to determine what research might lead to the development of more efficient agents for extinguishing fires in aircraft.

An analysis of the existing data was made with respect to the relative extinguishing effectiveness of different substances and the basic mechanisms involved in the action of extinguishing agents. Five basic actions of fire-extinguishing agents were enumerated and discussed. It appears that mechanical action, blanketing action, and chain-breaking action are the most important factors in extinguishing by gaseous and liquid agents.

Recommendations for research were made on the basis of the analysis. Information on the relative extinguishing effectiveness indicates that organic halogen compounds will most probably yield the more powerful extinguishing agents.

INTRODUCTION

The problem of reducing the fire hazard in aircraft is of paramount importance. If this hazard is to be minimized, maximum effectiveness in fire extinguishing must be achieved. Research and development in this field have been sponsored and conducted by the Civil Aeronautics Administration, the Air Force, the Bureau of Aeronautics, Department of the Navy, and other government and private laboratories. Although these investigations have been extensive, the majority have been predominantly applied rather than fundamental. Emphasis has been placed on such factors as methods of application of extinguishing agents, optimum rates of application, and minimum effective quantities required. A preliminary

survey of the aircraft-fire problem by the NACA Lewis laboratory staff (reference 1) indicates that a better understanding of the basic actions of fire-extinguishing agents is still needed.

It is generally assumed that the effect of fire-extinguishing agents can be explained on the basis of the following actions:

1. Cooling action, which lowers the temperature of the combustible below its ignition temperature
2. Blanketing action, which prevents air from reaching the fire and results in a dilution of the oxygen content of the surroundings
3. Mechanical action, which results from directing the agent across the fire with sufficient force to cut the flame away from the combustible

Studies in the recently developed field of chemical kinetics, however, indicate that certain substances are capable of exerting an inhibiting effect on the combustion reactions. This chemical action is not completely understood and has not yet been extensively utilized in the search for better fire-extinguishing agents.

A review of literature pertinent to fire-extinguishing agents was made at the NACA Lewis laboratory and is presented herein. The object of this review is to collect the widely scattered and heretofore unrelated facts concerning extinguishing agents, and to appraise and to correlate these facts in order to obtain some insight into the nature of the fundamental actions of extinguishing agents, particularly in regard to chemical actions as distinct from physical or mechanical actions. The ultimate aim of this review is to indicate regions in which further research would be advantageous to aid in the discovery of more powerful agents for extinguishing gasoline and oil fires in aircraft.

CRITICAL PRESENTATION OF DATA

Information pertinent to fire-extinguishing agents may be obtained from numerous widely diversified investigations, some of which have been conducted for the express purpose of studying fire-extinguishing phenomena. The majority of these investigations, however, have been conducted with other purposes in mind, the information applicable to fire extinguishing being incidental. Consequently, these data must be critically viewed before being applied to the problems of fire extinguishing.

For the sake of clarity, the most significant results are presented under the following six main headings; classification is made on the basis of the type of phenomenon under investigation:

1. Extinction of diffusion flames
2. Effect of additives on limits of inflammability of combustibles
3. Effect of additives on ignition temperatures of combustible mixtures
4. Effect of additives on velocity of propagation of flame in combustible mixtures
5. Direct application of fire-extinguishing agents to test fires
6. Kinetic studies of combustion reactions

Extinction of Diffusion Flames

The first experiments pertinent to fire extinguishing were probably the flame tests of Cavendish, Priestley, and others. (See references 2 and 3 for surveys of this early work.) These experiments consisted either in burning a jet of combustible gas in a closed vessel and analyzing the residual atmosphere at auto-extinction, or in plunging the flame into prepared mixtures of oxygen or air, and nitrogen or carbon dioxide. It was discovered in both cases that a limiting oxygen content existed, below which combustion could not be supported. This limit of oxygen content was found to be dependent on the nature of the combustible gas, on temperature and pressure, and when the extinguishing atmosphere was created by mixing oxygen or air with nitrogen or carbon dioxide, on the nature of the extinguishing gas. This dependence on the nature of the extinguishing gas is of interest in fire extinguishing and is discussed in a subsequent section.

A more practical procedure for investigating the effect of the extinguishing gas was developed by Rhead (reference 2) and adopted by Dufraisse and coworkers (references 4 to 7). The apparatus employed gas streams and consisted of a small burner, to which fuel could be supplied at any desired rate, placed coaxially in a large glass cylinder. Air, also supplied at any desired rate, was introduced at the bottom of the cylinder and flowed up around

the flame. The extinguishing gases or vapors to be investigated could be added in known amounts to the air feeding the flame, and it was therefore possible to determine the percentage of gas that must be added to cause extinction of the flame. The method permitted fine adjustment and control, and the flame could be studied in all its phases under varied conditions. The results, however, are sensitive to a number of experimental factors. (See references 2 and 8 for a more detailed discussion.)

Data obtained by Dufraisse, Vieillefosse, and Le Bras (reference 4) by using this method with a flame of illuminating gas are reproduced in table I. The authors drew the following conclusions from these data:

1. In general, the chlorides are less active extinguishers than the bromides, and the bromides are less active than the iodides.
2. The function of the halogen element is complex, as the activities of the substances have little relation to their halogen content.
3. The formation of the halogen acid or free halogen is not the cause of fire extinguishing by the halogen-containing substances.

It should be noted that gases and vapors that are inflammable in air under ordinary conditions are capable of extinguishing flames in the previously described apparatus, and that no attempt has been made to distinguish between those substances listed in table I that are inflammable and those that are not. This fact must be considered when appraising the preceding statements.

By using the previously described experimental procedure, Dufraisse and Le Bras (reference 5) investigated the mechanisms by which these substances extinguish a flame of illuminating gas under constant conditions. Information was obtained for the different extinguishing substances by sampling the residual gases of combustion when the flame was almost at the extinction point. The samples were taken at a point a few centimeters above the tip of the flame and were analyzed for oxygen, nitrogen, carbon dioxide, and carbon monoxide. Thus, it was ascertained that the extinguishers previously studied could be classified into two categories: (1) those that lower the residual oxygen content below that value necessary for extinction obtained when the inert gas, nitrogen, is used as the extinguishing gas, and (2) those that maintain it above this value. This classification seems rather arbitrary, but

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on that basis the investigators concluded that the substances of the group that maintained the oxygen content above that obtained for nitrogen, of which carbon tetrachloride is an example, function by inhibiting the combination with oxygen. The substances that maintained the oxygen content below that obtained for nitrogen, of which ethylbromide is an example, appear to increase the combination to the point where nearly all the ambient oxygen is consumed.

Le Bras (reference 8), using carbon tetrachloride and ethylbromide as examples of these two classes, extended these studies to flames of other combustibles. In a careful investigation of the experimental variables involved, he found that the percentage of carbon tetrachloride required for extinction varied erratically with the velocity of the air stream, and increased greatly with an increase in the velocity of the combustible gas. Ethyl bromide did not show such a variation. The dependence of the effectiveness of carbon tetrachloride on the velocities casts doubt on the significance of the results for the relative extinguishing efficiencies of the different substances given in table I.

In addition, Le Bras determined the percentages of carbon tetrachloride and ethylbromide necessary to extinguish flames of a number of combustible gases and vapors and also the percentage of residual oxygen in the combustion gases when the flame was maintained at a condition near extinction. For the sake of comparison, similar data were determined using the inert gas, nitrogen, as the extinguishing gas. These data are reproduced in table II. The percentage of oxygen in the extinctive mixture of nitrogen and oxygen is given in the fourth column. This percentage may be thought of as the minimum oxygen content, below which combustion cannot be supported. All percentages are on a volume basis.

An examination of these data shows that for carbon tetrachloride the extinguishing percentages vary greatly from one gas to another, yet no apparent connection exists between the extinguishing percentages of carbon tetrachloride and of nitrogen. As nitrogen probably acts simply as a diluent and coolant, Le Bras concluded that some additional actions must be involved in the case of carbon tetrachloride. The percentage of residual oxygen usually remained somewhat greater than the minimum oxygen content for the flames studied.

In the case of ethylbromide, the results are completely different. The proportion of extinguisher varied little, remaining

about 6 percent, and the residual oxygen content in the neighborhood of extinction was decreased to a value of approximately 2 or 3 percent.

Inasmuch as ethylbromide behaved the same toward flames of different combustibles, Le Bras studied in detail its effect on hydrogen. The use of hydrogen simplified the composition of the residual gases; any carbon dioxide or carbon monoxide found was attributable only to the ethylbromide, and it was relatively easy to determine the degree of decomposition or combustion of the ethylbromide. Le Bras determined the variation of the composition of the residual gas as a function of the ethylbromide that was added to the air stream. These results are depicted in figure 1.

From these results, Le Bras calculated that the ethylbromide was from 80 to 90 percent decomposed and that the proportion of hydrogen burned gradually diminished as the percentage of ethylbromide increased. He concluded that the ethylbromide carried on the extinction of the flame by consuming the oxygen and by forming a sheath of deoxygenated air around the flame. This method of extinction of a flame is similar to that observed in the case of inflammable vapors.

For carbon tetrachloride, the phenomena are much more complex, and the nature of the combustible is of prime importance. Detailed investigations were conducted with three different combustibles. In the case of a hydrogen flame, the results were complicated by reaction between the hydrogen and the carbon tetrachloride, which yielded hexachlorobenzene and tars. For a flame of illuminating gas, the results were complicated by the fact that the combustible was a mixture whose constituents contribute to the formation of carbon dioxide and carbon monoxide in the residual gas. Approximate calculations indicated, however, that carbon tetrachloride extinguished a flame mainly by a cooling effect, coupled with a slight inhibiting effect. In the case of a carbon-monoxide flame, the extinguishing percentage of carbon tetrachloride was quite small (2.5 to 3 percent). Analyses of the residual gases, with increasing amounts of carbon tetrachloride in the air stream, showed that the percentage of oxygen tended to increase slowly, to about 13 percent, although the minimum content necessary to support combustion was only 9.8 percent. Le Bras therefore concluded that the extinction produced must be by an inhibiting effect. This effect was especially pronounced if the carbon monoxide and the air were both dried; the extinguishing percentage of carbon tetrachloride was then only 0.65 percent.

Dufraisse and German (reference 9) investigated the extinctive effects of powders of several sodium and potassium salts on flames of different combustible gases and showed that the extinguishing effect of these salts cannot be fully accounted for only on the basis of cooling action and the possible liberation of an extinguishing gas by chemical decomposition in the flame. They used a simple arrangement of a flame placed coaxially in a glass cylinder. Air was introduced at the base of the cylinder at a velocity sufficient to carry along the powders but not sufficient to have any blowing-out effect on the flame. A lateral piston allowed projection at a desired velocity of a known dose of powder into the air stream. The results are presented in table III.

From these data, Dufraisse and German made the following observations:

1. The "supporters" of combustion (salts that can liberate oxygen upon decomposing) that are most sensitive to heat (KClO_3 , NaClO_3 , and KClO_4) behave either as activators of the combustion (hydrogen and illuminating gas flames) or as extinguishers (methane and carbon-monoxide flames), according to the temperature of the flame.
2. The supporters of combustion that are less sensitive to heat (KNO_3 and NaNO_3) extinguish all the flames tested.
3. Some of the supporters of combustion are better extinguishers than either the inert substances (talc and Na_2SO_4) or the substances that can liberate gaseous extinguishers (NaHCO_3 , KHCO_3 , $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$). For instance, potassium nitrate (KNO_3) is, according to the flame considered, from two to thirty-five times more active than sodium bicarbonate (NaHCO_3), the most highly reputed of the pulverized extinguishing agents in common use.
4. In spite of being more resistant to heat, potassium bicarbonate (KHCO_3) is much more efficient than sodium bicarbonate.

It was therefore concluded that the extent of decomposition of these salts in a flame is slight and that the extinguishing effect is caused primarily by some negative catalytic effect of the undecomposed salt.

Effect of Additives on Limits of Inflammability of Combustibles

In 1817, Humphrey Davy (reference 10) performed experiments concerning the influence of hydrogen chloride and silicon tetrachloride on the lower explosion limit of hydrogen and oxygen. Since that time, a great number of experimenters have investigated substances that can prevent the explosion of combustible gases and vapors in air. The first extensive search for such substances was begun by Jorissen (references 11 and 12) around 1920. It had been known for some time that many vapors of organic substances, even in small quantities, exerted a marked influence on the lower explosion limit of phosphorous, and Jorissen therefore concluded that similar substances might decrease the explosion limits of combustible gases and vapors. Working with methane-air mixtures, Jorissen (references 13 and 14) investigated the effect of various chlorine derivatives of methane, ethane, and ethylene on the limits of inflammability.

For his inflammability tests, Jorissen used small burettes, 25 centimeters long and 1.6 centimeters in diameter, placed in a vertical position. Platinum electrodes, placed 5 millimeters apart, were situated in the top of the burettes. Ignition was effected by a spark; propagation of the flame was in a downward direction. The effect of the chlorine derivatives on the limits of inflammability of methane was quite startling in comparison to the effect of the "inert" gases (helium, argon, nitrogen, and carbon dioxide); small additions produced a marked narrowing of the limits. Similar results were obtained with explosive mixtures of carbon monoxide and air, hydrogen and air, and acetylene and air (references 14 and 15).

In a direct attempt to find a substance that, when present in small quantities, would exert a complete retarding action on methane explosions, Jorissen (reference 16) investigated some 250 different substances. Fifty compounds, whose names were not given, were found that prevented explosion of a 10-percent methane-air mixture.

Jorissen showed, however, that information of this type was insufficient to pick effective extinguishing agents. In order to obtain a complete insight into the extinguishing effectiveness of a substance, the entire explosion region must be determined. Jorissen (references 16 and 17) determined this region for a number of the previously mentioned 50 substances, using burettes identical with those he had used in his experiments with the organic chlorine derivatives (references 13 and 14). He presented

his results in a simple graphical manner (fig. 2), in which the volume percentage of the added gas in the original atmosphere is plotted as a function of the volume percentage of the methane in the total mixture.

The figure for isobutylchloride shows the necessity of investigating the entire explosion region before conclusions can be drawn concerning the extinguishing effectiveness of a substance. Inasmuch as only 2 percent of isobutylchloride is necessary to prevent a 10-percent methane-air mixture from exploding, it would seem that this substance must possess a strong extinguishing action. Actually, the lower explosion limit of methane is extended by the isobutylchloride, which is inflammable itself between the limits of 4.1 and 14.2 percent. The curve for ethyliodide shows the characteristics of an effective extinguisher. Ethyliodide in a concentration of 5.3 percent prevents explosion in all possible methane-air mixtures.

This experimental procedure and graphical representation offers a method by which a quantitative measure of the relative extinctive effectiveness of different substances can be obtained. It is necessary only to determine the percentage of the given substance required to render noninflammable all mixtures of some given combustible substance in air. Those substances that are required in the smallest percentages are the most effective. The different substances investigated by Jorissen are arranged in table IV in order of decreasing effectiveness. The volume percentages in the original atmosphere necessary to prevent explosion in all methane-air mixtures are also given. These results show that certain halogen-containing compounds have a greatly enhanced aptitude for provoking extinction when compared with the inert gases.

In the course of investigations pertaining to the promotion of safety, the Bureau of Mines in the United States and the Safety in Mines Research Board in England have done a considerable amount of work on the limits of inflammability of gases and fuels. This work has included studies of the effects of certain additives upon these limits.

The first study was that of Coward and Hartwell (reference 19) on the effect of the inert gases on the inflammability limits of methane-air mixtures. The limits were determined in an atmosphere of ordinary air, mixed with increasing amounts of the added gas. The design of the apparatus used for determining the inflammability limits was based on the results of Coward and Brinsley (reference 20), obtained in their classical experiments on the limits of

inflammability of combustible mixtures. The apparatus consisted of a vertical pyrex tube 180 centimeters long and 5 centimeters in diameter. The bottom end was covered with a ground glass plate. Ignition was effected from below by sliding back the plate and passing a small alcohol flame across the opening. A given mixture was considered inflammable if the flame traveled to the top of the tube. Coward and Brinsley defined inflammability as the property of a mixture to propagate a flame indefinitely, and showed that inflammable limits, determined as previously explained, were a property only of the mixture; that is, they were independent of the shape and size of the containing vessel and of the means used for ignition. (See reference 20 for a complete discussion.)

The results of these experiments, along with the results of other work done by the Bureau of Mines and the Safety in Mines Research Board on the influence of additives on methane-air mixtures, are given in table V. Identical apparatus was used in all this work. In table V, the gases are arranged in order of decreasing extinguishing effectiveness as measured by the volume percentage of added gas in the original atmosphere necessary to bring the limits into coincidence. Coward and Hartwell (reference 19) concluded that the relative extinguishing effects of carbon dioxide, nitrogen, and argon could be explained in the basis of their relative heat capacities, the gas of greater heat capacity having the greater extinguishing action. The abnormal behavior of helium, which has a heat capacity equal to that of argon, was ascribed to its exceptionally high heat conductivity. As a result, these investigators concluded that the following factors were mainly responsible for the extinction of flame: (1) reduction of oxygen content by diluent gas (primarily affects the upper limit), (2) thermal capacity of diluent, and (3) thermal conductivity of diluent.

The position of water in this table indicates that it too probably extinguishes primarily by a cooling action. Carbon tetrachloride and dichlorodifluoromethane illustrate that certain halogen-containing compounds have a greatly enhanced aptitude for provoking extinction, as shown by Jorissen. A comparison of these results with those of Jorissen (table IV) shows that the percentages necessary to prevent inflammation in all methane-air mixtures obtained by the Bureau of Mines are larger than the percentages obtained by Jorissen. Coward and Jones (reference 21) severely criticized the small apparatus and experimental technique used by Jorissen. In part, this criticism seems justified. It is certain that with the small diameter tube (1.6 cm) used by Jorissen, the cooling effect of the vessel walls was not eliminated. Also, because of the short length of the tube (25 cm), the flame was not

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given a long enough "run" to enable observers to judge whether it was self-propagating when it had lost the initial impulse due to the source of ignition. In addition, Jorissen used downward propagation of the flame rather than upward propagation. All these factors tend to make the inflammable region smaller, and thus result in a smaller value for the percentage of extinguishing gas than is necessary to prevent inflammation. Jorissen's tests therefore did not give a true measure of the inflammability of the mixture, but were a function of the apparatus. Nevertheless, the results are consistent within themselves, inasmuch as identical apparatus was used in all the determinations. As a result, their use for a comparison of the extinguishing action of the substances studied is not invalidated.

The Bureau of Mines investigated the effects of additives on the inflammable limits of many combustible gases other than methane (reference 24). These results are summarized in table VI. The extinguishing effect is expressed as the volumes of extinguishing gas necessary to render noninflammable one volume of combustible gas under all conditions. The last column, which shows the relation between the volumes of carbon dioxide and nitrogen required to produce noninflammable mixtures, is of special interest. All these ratios are close to the average value 0.57 for the various combustibles investigated. An explanation of this fact is found in the thermal theory of extinction suggested by Coward and Hartwell (reference 19). If it is assumed that the flame-propagating temperature for the different combustibles is 1400° C, the mean molar heat capacity between 25° and 1400° C can be calculated to be 7.46 calories per °C for nitrogen and 11.85 calories per °C for carbon dioxide. If the extinctive effect of the added gas is due entirely to its heat-absorbing capacity, then the relative efficiency of the two gases for extinguishing flames should be proportional to their heat capacities and inversely proportional to the volumes required to extinguish one volume of the combustible. The ratio of the heat capacities for nitrogen and carbon dioxide is 0.63, in close agreement with the average ratio of the volumes given in table VI, which seems to confirm the thermal theory of flame extinction in the case of nitrogen and carbon dioxide for a large variety of combustibles.

An extensive investigation in search of more effective fire-extinguishing agents was recently conducted at Purdue University. The same procedure was used as that developed at the Bureau of Mines. The combustible used was n-heptane mixed with air. Experiments were conducted with pressures in the explosion tube ranging from 300 to 500 millimeters of mercury. Jones

and Kennedy (reference 25) have shown that the inflammable limits of natural gas (79.6 percent CH₄, 19.2 percent C₂H₆, and 1.2 percent N₂ by volume) are scarcely changed by reduction of pressure to values as low as 200 millimeters of mercury. It was assumed that heptane would behave similarly. The results of the Purdue University investigation, as of August 1948, are given in table VII. Substances are arranged in order of decreasing effectiveness.

The following conclusions were drawn from the data obtained from the Purdue University investigation:

1. Within a series of similar compounds, the extinctive efficiency increases with the molecular weight. This increase is illustrated by the following compounds:

Compound	Molecular weight	Percent by volume
CF ₄	88	26
C ₂ F ₆	138	13.4
C ₄ F ₁₀	238	9.8
C ₇ F ₁₆	388	7.5

The relation is not linear, but levels off with increasing molecular weight.

2. The relative effects of halogen substitution on extinction properties follows the series I > Br > Cl > F, which is illustrated by the following compounds:

Compound	Percent by volume	Compound	Percent by volume	Compound	Percent by volume
CF ₄	26	CH ₃ Br	9.7	CH ₂ Cl ₂	high
CClF ₃	12.3	CH ₃ I	6.1	CH ₂ BrCl	7.6
CBrF ₃	6.1			CH ₂ Br ₂	5.2

Inasmuch as the following exceptions to the generalization expressed in the second conclusion exist;

Compound	Percent by volume	Compound	Percent by volume
CHF ₃	17.8	CClF ₂ CHBrCH ₃	6.4
CF ₄	26	CF ₃ CHBrCH ₃	4.9

it may be that certain groupings are more effective than others. For example, $-\text{CF}_3 > -\text{CHF}_2 > -\text{CClF}_2 > -\text{CBrF}_2$.

Effect of Additives on Ignition Temperatures of Combustible Mixtures

Considerable research has been conducted concerning the effects of additives on the ignition temperatures of combustible gaseous mixtures. Certain substances, when added in small amounts to such mixtures, produce a decrease in the inflammability of the mixture, as indicated by an increase in the ignition temperature.

In England, the Explosives in Mines Research Committee has sponsored the search for such substances. The first results reported were those of Dixon (reference 26). Dixon, upon a suggestion of Richard Vernon Wheeler, investigated the effect of ethyliodide on the ignition temperature of methane. It was found that the ignition temperature of a fire damp-air mixture (in a closed silica vessel) was raised 125°C (from 634° to 759°C) by the addition of ethyliodide in a concentration of two parts per thousand. In addition, it made no difference whether the iodine was introduced as free iodine, ethyliodide, or any other compound containing iodine. Nearly similar effects were obtained with a bromide.

These investigations were extended in parallel experiments by Naylor and Wheeler (reference 27) and by Coward (reference 28). Naylor and Wheeler employed an experimental method whereby an inflammable mixture was rapidly admitted to an evacuated vessel of quartz heated to the desired temperature. The lowest temperature of the reaction vessel that caused the mixture to inflame, no matter how long after its admission, was recorded as the ignition temperature of the mixture. The results on the effects of various additives are summarized in table VIII. These results were all obtained with a 5.8-percent methane-air mixture.

Each of these substances raised the ignition temperature, the degree of elevation varying with the amount present. In table VIII, the maximum ignition temperature is recorded, with the amount of substance that produced it.

The "concentric-tube" apparatus of Dixon and Coward proved more suitable for investigations of this type. In this apparatus, a stream of combustible gas is passed up a heated tube fixed in

the axis and opening into the center of a large silica cylinder up which a stream of air or oxygen is flowing. A furnace surrounds this cylinder so that the air may be heated to the same temperature as the fuel. In an experiment, the flow of combustible gas is not started until the air stream has attained the desired temperature. With this procedure, the time lag for ignition can be measured. Ignition occurs at the point of mixing of the gas streams; the measured ignition temperatures therefore are not influenced by effects taking place on the walls of the vessel, which is a desirable condition. The inhibitors to be studied are added to the air stream.

Dixon and Coward investigated the effect of iodine on the ignition temperatures of methane, hydrogen, and carbon monoxide. The results for methane, which were typical, are plotted in figure 3.

For methane, the optimum increase in the ignition temperature (approximately 70° C) occurred at an iodine concentration of about 0.03 percent, although 0.01 percent was nearly as effective. With hydrogen in air, the effect of 0.01- to 0.03-percent iodine was less marked, but addition up to 0.15 percent raised the ignition temperature about 70° C. In the case of carbon monoxide (dry), the ignition temperature rose more rapidly than with hydrogen, and with 0.062-percent iodine was beyond the limit of the furnace (928° C), which amounted to a rise of more than 230° C.

The ignition points of methane in air containing ethyliodide were also investigated, but did not show much resemblance to those in air containing free iodine. The highest point, however, was the same and occurred for the same concentration of iodine. This same maximum temperature was also obtained using methyl iodide.

The ignition points of methane in air containing ethylenebromide, isoamylbromide, and bromobenzene were determined. The results are reproduced in figures 4, 5, and 6, respectively.

These substances behaved as powerful inhibitors. Their effects were nearly equal for an equivalent concentration of bromine up to about 0.1 percent, at which point the increase in ignition temperature was about 100° C. It therefore appears that bromine is more efficient than iodine. Further small additions of bromine compounds to the air produced a small rise in ignition temperature; but with greater amounts, the three inhibitors differed in that ethylenebromide had a maximum effect at a concentration of about 0.3 to 0.4 percent; whereas the other two inhibitors

continued to show an increasing effect. The difference was explained by the interaction of the inhibitors with the oxygen of the air before the atmosphere reached the jet. The large rise of ignition temperature when only 0.1 or 0.2 percent of the bromide was present in the air must, however, be almost entirely due to the bromine.

As a result of Jorissen's experiments with phosphoryl chloride (reference 17), Dixon and Coward also investigated the effect of this compound (reference 28). It was found that phosphoryl chloride raised the ignition temperatures of the methane, but that the maximum increase was less than half (about 45° C) that of the bromine compounds. The maximum occurred at a concentration of about 1 percent of phosphoryl chloride.

Tetraethyl lead was investigated because of its strong anti-knock characteristics. The curves were of the same type as those of isoamylbromide and bromobenzene, and were interpreted in the same way. The inhibitory effect, however, was found to be only about one-half that of the bromine compounds, although the increase with concentration was about the same.

Dixon and Coward also investigated the effect of the inert gases, nitrogen and carbon dioxide, on the ignition temperature of methane. These gases caused an increase in the ignition point, as would be expected, but the effects were very small in comparison with the increase produced by traces of bromine compounds and iodine.

Certain metallic salts have a marked effect upon the ignition of combustible gaseous mixtures. For instance, it has long been known that the gas from a blast furnace can be burned regularly only after elimination of the potassium salts that it holds in suspension. Also, sodium and potassium salts have long been used as antflash substances for preventing artillery muzzle flame.

Prettre (reference 29) showed that small concentrations of alkali halide salts raised the ignition temperature of carbon monoxide - air mixtures. Jorissen and coworkers (references 30 to 32) investigated the effects of powders of 140 different substances on 10-percent methane-air mixtures. They found that the best substances for preventing explosion were the halides and carbonates of sodium and potassium. Halides of calcium and barium were also fairly effective.

Muraour and Michel-Lévy (reference 33) have shown that this extinguishing effect of alkali metal salts is due primarily to

some specific action of the salt, and not just to a cooling effect. A combustible gaseous mixture was produced by combustion of powdered nitrocellulose in a Vieille type bomb. The approximate composition of the gas was: 35-percent carbon monoxide, 17-percent hydrogen, 17-percent carbon dioxide, 11-percent nitrogen, and 20-percent water. In this type bomb, the products of combustion escape through a 1-millimeter hole and normally ignite upon contact with the air. Muraour investigated the effect on the ignition of picrates of the alkali metals, the alkaline earths, and the heavy metals. Picrates were chosen because they are explosive. The salt was mixed with the nitrocellulose and, when exploded, liberated the metal at a high temperature, thereby eliminating the cooling action of the salt. Muraour found that 10 percent of potassium picrate sufficed to prevent all inflammation of the escaping gas. Of the other picrates studied, only those of rubidium and cesium showed any antifiame action. Muraour concluded that the extinguishing effect in this case was due to some action of the alkali metal.

Effect of Additives on Velocity of Propagation of Flame in Combustible Mixtures

A completely satisfactory theoretical treatment of the velocity of flame propagation is still forthcoming. It is clear, however, that the velocity of the chemical reaction involved is of decided importance. Consequently, the effect on the velocity of propagation of flame offers a method of investigating substances suspected of being inhibitors of the combustion reactions. This method has been confined almost entirely to the investigation of the effects of antiknock substances.

Antiknock substances appear to be powerful inhibitors of the slow oxidation reactions of most hydrocarbons, but their use in fire extinguishing is limited because they are highly inflammable and, when present in high concentration, the free radicals that are liberated probably accelerate the fast oxidation reactions occurring at high temperature. It is possible, however, that antiknock substances might be useful in fire extinguishing if added in small amounts to other extinguishing agents.

The only substance possessing fire-extinguishing potentialities that has been investigated by its effect on the velocity of propagation of flame is phosphoryl chloride. Jorissen (reference 34) has reported some results of Coward on the effect of phosphoryl chloride on the velocity of flame propagation in a 9.8-percent methane-air mixture; these results are presented in table IX.

It is evident that phosphoryl chloride has a marked decelerating effect upon the flame speed.

Direct Application of Fire-Extinguishing Agents to Test Fires

The most direct method of investigating the fire-extinguishing potentialities of different agents is by direct application to test fires. Extensive investigations of this type have been conducted. The CAA has recently run a series of tests on fires under simulated flight conditions in different radial-type aircraft engines (reference 35). The purpose of these tests was to determine the efficiency of various fire-extinguishing agents when applied to gasoline and oil fires occurring in both the power and accessory sections of aircraft power plants, and to determine for each agent the quantity required, the rate of application necessary, and the optimum methods of distribution. Eight different extinguishing agents were investigated under conditions of comparable rates of application. With respect to extinguishing effectiveness, the results given in table X were obtained.

Concerning these results, the following statement is made in reference 35: "This method of comparison is essentially qualitative, as attempts made to compare the agents on a quantitative basis could only be approximate." Perhaps a more quantitative comparison is obtained from the data given in table XI taken from the same report. It appears from this table that methylbromide is a better extinguishing agent than carbon dioxide or the other agents.

The German navy and air forces (reference 36) made similar investigations with a commercial mixture of monochlorobromomethane consisting of 82-percent monochlorobromomethane, 9-percent methylenechloride, and 9-percent methylenebromide, which was mixed with carbon dioxide in percentages of 65 to 35, respectively. These investigations showed that only 12- to 15-percent concentration was required to extinguish a standard gasoline wind-tunnel test fire, which compared with 45-percent concentration required for carbon dioxide alone and 15-percent concentration of methylbromide. Thus, monochlorobromomethane seems to be slightly better than methylbromide as a fire-extinguishing agent, and both are better than carbon dioxide.

The C-O-Two Fire Equipment Company conducted laboratory investigations (reference 37), the results of which indicate that monochlorobromomethane is many times more effective as an extinguishing agent than either carbon tetrachloride or Pyrene. Small pan

fires of gasoline were used as test fires, and were extinguished by using a laboratory wash bottle and a 1-quart, standard hand fire extinguisher. The pans were placed in a hood, the ventilating fan of which was cut off during the fire test. The results are given in table XIII. These results are only semiquantitative at best, but show that monochlorobromomethane is a better extinguishing agent than carbon tetrachloride.

Oliver C. de C. Ellis (reference 38) has recently conducted experiments to determine the fire-extinguishing potentialities of methyl iodide. He found that in all cases where carbon tetrachloride was effective, methyl iodide was equally effective, but with only one-fifth of the quantity required for carbon tetrachloride. In experiments with large water-borne gasoline fires (40 sq ft and more), carbon tetrachloride was a complete failure, as was a saturated water solution of ammonium iodide and methylene iodide. These substances burned in the flames. Under a spray of methyl iodide, however, the gasoline flames broke, wilted, and withered. Pan fires of ether, methylated spirits, and white spirit, which could not be extinguished by carbon tetrachloride, were swiftly quelled by methyl iodide, indicating that methyl iodide is much more effective than carbon tetrachloride as an extinguishing agent.

The experiments cited are but a fraction of those that have been performed. They include, however, most of the compounds that have been tested by direct application, and from them the different extinguishing agents may be arranged in a general way according to their fire-extinguishing effectiveness. In order of decreasing effectiveness they are: methyl iodide; monochlorobromomethane; methyl bromide; carbon tetrachloride; carbon dioxide; and sodium and potassium carbonates. Although methyl iodide has been compared only to carbon tetrachloride, it has been placed above monochlorobromomethane and methyl bromide because it appeared so much more effective than carbon tetrachloride.

In the Purdue University investigation, experiments were performed with several gaseous extinguishing agents in conjunction with the inflammable-limits experiments. A small iron cup was used, filled to about one-half its capacity with *n*-heptane, placed within a 1-liter beaker. A sample of the gaseous agent was collected over water in a graduated cylinder. The heptane was ignited and the extinguishing agent was introduced at the bottom of the beaker at a constant rate. The volume of the gas required to put out the fire was measured, and the results are presented in table XIII. The volumes of the gaseous materials represent the average of

several determinations. It is evident that methylbromide is more effective than carbon dioxide when both are applied as gases.

The experiments of Thomas and Hochwalt (reference 39), although performed some 20 years ago, still remain as the only investigations in which comparative values of extinguishing agents have been measured in a quantitative manner by using the method of direct application to test fires. Known quantities of all the water-soluble metallic salts were dissolved in water, and the influence these salts had on the fire-extinguishing effectiveness of water in quenching gasoline fires was investigated. The apparatus consisted of a light metal fire pan mounted on an adjustable platform and placed inside a metal hood, which served to exclude drafts. A thermocouple was placed in the back of the pan above the gasoline level. A test extinguisher, which discharged the extinguishing agent under a constant pressure of nitrogen, was also mounted in the hood. Fires were started by throwing a lighted match onto the gasoline, and the result of a test was considered to be positive if the fire was extinguished. The test was repeated with solutions of various concentrations until the minimum concentration that gave a positive result was determined. By giving special attention to leveling the fire pan and aiming the extinguisher, by carefully filling the pan to the same level in each test, by always allowing the thermocouple to heat up to the same temperature (270° C) before turning on the extinguishing agent, and by carefully cleaning and drying the fire pan between tests, Thomas and Hochwalt were able to obtain satisfactory reproducible results, which are presented in table XIV.

These results were quite unusual. The investigators found that the extinguishing qualities of water were greatly enhanced by salts of the alkali metals, but were unaffected by salts of the other metals. Also, the effectiveness increased with the atomic weight of the alkali metal present, as shown in table XV. Furthermore, the effectiveness of the alkali metal salts was decidedly influenced by the nature of the radical attached to the alkali metal. Peculiarly, radicals that have oxygen in them have a greater extinguishing effect than those without oxygen. Some examples of this effect are given in table XVI. From this fact, plus the fact that potassium permanganate and dichromate are among the most effective potassium salts, it appeared that any oxidizing agent might demonstrate this enhancing effect upon the extinguishing qualities of water. Tests with iodic acid, perchloric acid, and chromic acid, however, gave only negative results, although concentrations as high as 10 normal were used. It therefore seems that the alkali metal is essential to this extinguishing effect.

Organic compounds, as a rule, were very effective extinguishers, and the degree of their effectiveness was proportional to their oxygen content. For example, the bitartrate of potassium was five times as effective as the neutral salt. The investigators were unable to explain these phenomena, and ascribed them to some chemical or catalytic action.

Rakuzin (reference 40) obtained results consistent with the preceding results. He found that oil fires were readily extinguished by the action of 6- to 8-percent solutions of sodium and potassium carbonate; whereas solutions of ammonium carbonate, calcium chloride, barium chloride, sodium chloride, ferric sulfate, alum, and ammonium hydroxide had no effect.

Kinetic Studies of Combustion Reactions

A large number of kinetic studies have been made of many of the simpler combustion reactions. Some of these studies have included investigations of the inhibiting effect of certain substances.

Hinshelwood and coworkers (references 41 to 44) made an exhaustive study of the reaction between hydrogen and oxygen. The hydrogen-oxygen combination is one of the best examples of a reaction depending upon branching chains and showing the phenomenon of explosion limits. In the region of 550° C, this reaction exhibits three explosion limits, the first at a pressure of a few millimeters, the second at about 100 millimeters, and the third at several hundred millimeters. Below the first limit, the reaction rate is negligibly small; between the first and second there is explosion; above the second limit, explosion gives place to slow reaction, which rapidly increases in rate as the pressure is raised until at the third limit there is explosion once more. The effect of halogens on the reaction in the low-pressure explosion region and on the rapid reaction above the second explosion limit were investigated (references 41 and 42). In the first case, it was found that small quantities of a halogen rapidly reduce the size of the explosion region, and then eliminate it altogether. Iodine eliminates all explosion when present in a concentration of 0.0022 percent or greater; bromine eliminates all explosion when present in a concentration of 1 part in 10,000; chlorine is much less efficient, a concentration of about 1 part in 400 being needed. In the second case, that of the high pressure reaction, there is also an inhibition by halogens. At 550° C and a pressure of 450 millimeters (H₂, 300 mm; O₂, 150 mm), the following reductions in reaction rate were effected by iodine:

Concentration of I ₂ , (mm Hg)	Rate of reaction Δp, (mm/min)
0	35
0.0033	14
.017	5.4
.033	5.0
.10	5.4
.17	5.2
.33	6.3
.83	8.0
1.33	11.4

Similar, although not as marked, results were obtained with bromine and chlorine. It is evident that as the partial pressure of the halogen is increased, the reaction velocity is at first drastically reduced, passes through a minimum and then slowly increases, but the value of the velocity always remains smaller than it would be with a simple hydrogen-oxygen mixture.

The mechanism of the hydrogen-oxygen reaction is fairly well established and is of the branched-chain type. Hinshelwood explained that the action of the halogen inhibitors is due to the removal of the chain carriers by the simple reaction



The reason for the smaller efficiency of chlorine is that the reaction



can regenerate a hydrogen atom; whereas the corresponding process is very improbable with bromine and iodine.

The existence of a minimum in the curve of reaction rate against halogen concentration was shown, by use of reaction bulbs with different surface-volume ratios, to be due to the acceleration by the halogen of the heterogeneous reaction occurring on the walls of the vessel. Thus, the action of the halogen is two-fold: (1) It inhibits the homogeneous gas-phase reaction by removal of the hydrogen atoms; and (2) it accelerates the heterogeneous reaction occurring on the walls.

Similarly, Hadman, Thompson, and Hinshelwood (references 43 and 44) showed that minute amounts of iodine exert a strong inhibiting action in the homogeneous reaction between oxygen and both

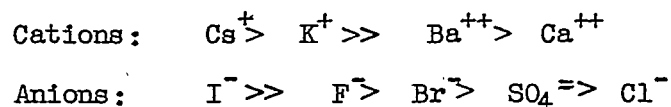
moist and dry carbon monoxide. Norrish and Foord (reference 45) have shown that at temperatures above 500° C iodine acts as a powerful anticatalyst to the ignition of methane. These reactions also show the characteristics of branched-chain mechanisms, and the action of the iodine has been interpreted as one of removal of the chain carriers.

The influence of various salts on the combustion reactions has been investigated by coating the surface of the reaction vessel with a coherent layer of the salt under investigation. Pease (reference 46), while studying the slow oxidation of propane and butane, observed a notable increase in the temperature at which these gases commenced to oxidize noticeably when the walls of the reaction vessel were covered with potassium chloride.

Jorissen (reference 47) investigated the influence of coatings of the alkali halides on methane-oxygen mixtures. He measured the temperatures at which carbon dioxide could first be detected after heating the mixtures for 1/2 hour. The lowest temperature at which reaction occurred was 170° C, with a coating of lithium fluoride; and the highest temperature was 540° C, with a coating of potassium iodide. The uncoated tube gave reaction at 250° C. The temperature of observable reaction was found to rise in the order Li, Na, K, Rb, and F, Cl, Br, I.

Willbourn and Hinshelwood (reference 48) investigated the influence of different salts on the hydrogen-oxygen reaction. The first and third explosion limits depend upon the surface, and were profoundly affected; but the second limit, which is controlled by a gas-phase process, was not affected. The results obtained for the first limit are given in table XVII.

It is known that the first explosion limit is determined by chain-breaking at the walls. As a result, the data of table XVII may be taken as a measure of the relative chain-breaking efficiencies of the various salts. The following relative efficiencies of anions and certain of the cations in contributing to chain-breaking were obtained:



The effect of the iodide ion was particularly marked.

The results obtained on the reaction above the second limit and on the third explosion limit were more complex. Lewis and von Elbe found that salts as different as barium chloride, potassium chloride, potassium metaborate, and sodium tungstate had practically identical actions (reference 48). They concluded that the limiting condition had been reached when the chain-breaking efficiency of the surface was unity. On this hypothesis, it was expected that a number of salts could be found that would behave in a similar fashion, and that no salt would depress the reaction rate more than potassium chloride. The results of Willbourn and Hinshelwood, given in the following table, did not verify this theory:

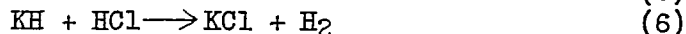
Temperature, 550° C; pressure, 450 mm Hg (H₂, 300 mm; O₂, 150 mm)

Salt	LiCl	NaCl	KCl	RbCl	CsCl
Rate (mm/min)	0.65	0.90	0.60	0.60	0.28

It is evident that cesium chloride (CsCl) depressed the rate of reaction appreciably more than any of the other chlorides.

Additional results are reproduced in figure 7. From the preceding table and figure 7, it is seen that the diversity of behavior among the salts was considerable and that the relative effects of two salts might be different at different temperatures.

It is known that the hydrogen-atom concentration controls the rate of branching in the region of the first explosion limit. In the region of the third limit, destruction of HO₂ is important. If HO₂ reacts with a hydrogen molecule on the surface to give H₂O₂ + H, then the subsequent fate of the hydrogen atom so formed may also determine the observed chain-breaking characteristics of the surface at these higher pressures. In addition, the salts with chain-breaking effectiveness all contained cations (alkali metals and alkaline earths) that can form hydrides. As a result, Willbourn and Hinshelwood postulated transformations of the following type to explain the chain-breaking action of the salts:



Hydrogen atoms can therefore be removed without a permanent change of the salt. The large effect of iodides was explained by postulating the liberation of minute amounts of iodine, which break the chains in the gas phase.

ANALYSIS OF DATA

Information on fire-extinguishing agents may be classified loosely into two major categories in order to facilitate discussion: (1) information on the relative extinguishing effectiveness of different substances, and (2) information on the actions of fire-extinguishing agents.

Relative Extinguishing Effectiveness of Different Substances

Gaseous and liquid substances. - The most positive method of obtaining information on the fire-extinguishing effectiveness of different substances is obviously by direct application to test fires. As previously pointed out, however, the results obtained by this method have been predominantly qualitative in nature. The method has been used in determining, for the more common extinguishing agents, the optimum conditions for extinguishing different types of fire. With the exception of the work of Thomas and Hochwalt (reference 39), which was limited to water-soluble salts, the method has not been used for a quantitative determination of the relative efficiencies of substances suspected of possessing fire-extinguishing potentialities. As a result, such information must be obtained from other sources.

The investigation of the effect of additives on the inflammable limits of combustibles offers a method by which a quantitative rating of different gaseous and liquid extinguishing agents may be obtained. In measurements of this type, however, the mechanical action of the extinguishing agent is inoperative and the blanketing action is eliminated except for some diluting effect, which is smaller as the agent is more effective. Nevertheless, the cooling action and the chemical actions are fully operative. The rating of compounds obtained by this method is therefore only on the basis of cooling and chemical actions. These are important actions and the results are quite valuable.

Flame-speed studies should yield results analagous to inflammable-limits studies because the limits of inflammability are largely determined by the velocity of propagation of the flame.

Little data obtained by this method are available, however, which is undoubtedly due to the difficulty involved in making precise, reproducible measurements of flame speeds.

A fairly quantitative rating of gaseous and liquid extinguishing agents may be obtained from diffusion-flame studies. Le Bras (reference 8), however, has shown that, for carbon tetrachloride, the results are an unknown function of the velocity of the gas and air streams. This situation probably exists for many other substances also, so that relative ratings obtained by this method are not very significant.

Results obtained from ignition-temperature studies on gaseous and liquid substances are probably not too reliable. It is known that the ignition temperature of a given combustible is a complex phenomenon and cannot be regarded as a physical constant. It is a function of many variables, and any determination of it is an empirical procedure. In particular, the ignition temperature is a complex function of pressure; consequently, the effects that additives produce are also affected by pressure. For example, Townend, Cohen, and Mandlekar (reference 49) have shown that 0.05-percent tetraethyl lead will raise the ignition temperature of a 2.7-percent pentane-air mixture 26° C at 1.0 atmosphere, and 171° C at 1.75 atmospheres. In addition, Schaad and Boord (reference 50) have shown that the effect of additives is a function of the composition of the combustible mixture, so that an additive may increase, decrease, or have no effect on the ignition temperature, depending on the composition of the combustible mixture involved. Inasmuch as the ignition temperature is so dependent on the conditions under which it is determined, it seems necessary to confine the use of ignition-temperature data to only a qualitative indication of fire-extinguishing potentialities.

It may therefore be concluded that the only available information on which to base a reliable rating of the fire-extinguishing potentialities of different gaseous and liquid substances are the results obtained by direct application to test fires and from inflammable-limits studies. The results obtained by the direct method are qualitative in nature and only a few compounds have been investigated. As a result, little correlation can be made between the fire-extinguishing effectiveness of a substance and its physical and chemical properties. The results of the inflammable-limits studies are quantitative, but measure only the effect of cooling and chemical actions. These actions, however, are dependent on the physical and chemical properties of the different substances and the following conclusions may be drawn from these data for the different extinguishing agents:

1. The "inert" gases (helium, argon, nitrogen, water vapor, and carbon dioxide) are the least effective of the fire-extinguishing agents.
2. Many substances are much more effective than the inert gases; practically all these substances contain halogen elements.
3. For analogous organic compounds, the effectiveness increases markedly, going up the halogen series F, Cl, Br, I.
4. For a given homologous series, there are indications that the effectiveness increases with increasing molecular weight, markedly at first and slightly thereafter.
5. For isomeric alkyl halides, there are indications that the isomer with a secondary-bonded halogen is more effective than the one containing the primary-bonded halogen. No data are available on tertiary-bonded halogen.

Metallic salts. - The metallic salts have been used as fire-extinguishing agents both in water-solution and in powdered form. The relative effectiveness of the different salts appears, however, to be the same in either case. The results of Thomas and Hochwalt (reference 39) with water solutions show that only salts of the alkali metals exhibit any degree of fire-extinguishing ability and that the effectiveness is largely determined by the alkali metal, increasing in the order Li, Na, K, Rb, Cs. The effectiveness also varies with the radical attached to the metal and seems to be greatest for radicals containing oxygen (Cr_2O_7^- , MnO_4^- , IO_3^- , $\text{C}_4\text{H}_6\text{O}_4^-$, and so forth) and for the halides. These results were obtained by direct application to test fires and are quantitative in nature.

The applications of powders or dusts to fire extinguishing are limited because they settle out of the atmosphere fairly rapidly and their extinguishing value is thereby lost. The results of the CAA (reference 35), obtained by direct application to test fires, rate powdered sodium and potassium carbonate as less effective than the common gaseous and liquid extinguishing agents. No data obtained by this method are available for determining the relative effectiveness of the different powdered salts. All the information obtained by the other methods indicates, however, as in the case of the water solutions, that the presence of an alkali metal is essential and that the effectiveness increases with the atomic weight of the metal atom. The influence of the radical involved is not so definite, and different experimenters report

contradictory results. The results of Willbourn and Hinshelwood (reference 48) and of Dufraisse and German (reference 9) indicate that the effectiveness of a salt is probably dependent on flame temperature. This dependency may explain the discrepancies in the order of effectiveness of the radicals obtained by different methods.

Actions of Fire-Extinguishing Agents

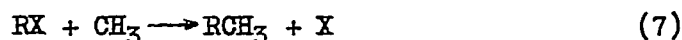
Nature of actions. - The actions by which extinguishing agents put out fires may be classified into two main groups: (1) physical actions, and (2) chemical actions. The physical actions include mechanical action, blanketing or diluting action, and cooling action. These actions are described in the INTRODUCTION. The chemical actions include: (1) chain-breaking, and (2) "preferential-oxidation." These actions are described in the following section.

The chemical actions are complex. A complete understanding of them ultimately depends on a complete understanding of the combustion mechanisms. In the case of the hydrocarbon compounds, which are chiefly considered, the combustion processes are so intricate and complex that a rational scientific solution of them is impossible at present. It has been fairly well established, however, that hydrocarbon combustions, like the hydrogen and carbon-monoxide combustions, proceed by branched-chain mechanisms, although it is not known with certainty what radicals function as the chain carriers. The inhibiting action that minute quantities of the halogens and other substances have on these reactions can be explained on the basis of this theory. The action of the inhibitors has been interpreted as one of combination with or deactivation of the chain carriers, resulting in a breaking of the reaction chains and a subsequent partial or complete retardation of the reaction. This chain-breaking action is the more important of the two chemical actions of fire-extinguishing agents. The other chemical action, preferential oxidation, which is exhibited by some of the slightly inflammable extinguishing agents, is the reaction of the agent with the ambient oxygen and results in a smothering of the fire.

Little specific information is available concerning the nature of the chemical actions. Le Bras (reference 8) shows that ethylbromide, which is slightly inflammable in air, acts to some extent by combining with the ambient oxygen. Coward and Dixon (reference 28) show that isoamylbromide, which is more inflammable than ethylbromide, behaves similarly but also exerts a strong inhibiting

effect. Le Bras reports that carbon tetrachloride exerts an inhibiting action on the combustion processes, the magnitude of which depends on the combustible. The exact nature of this inhibiting action is difficult to describe without a knowledge of the chain carriers involved in the combustion reactions.

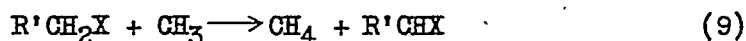
A. van Tiggelen, of the National Institute of Mines, Liège, Belgium, attempted a theoretical treatment of the inhibition of the combustion of methane by alkyl halides. He assumed that the methyl and hydroxyl radicals are the most important chain carriers and that inhibition is effected by chain-breaking reactions of the type



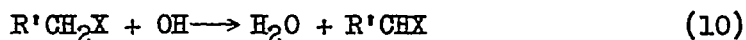
and



in competition with reactions of the type



and



which substitute one radical for another, but do not break the chain. He was able to draw only qualitative conclusions from his treatment because of lack of knowledge of the activation energies of the reactions assumed and the amount of dissociation of the alkyl-halide compounds in the flame region. He therefore concluded that alkyl bromides should be better inhibitors than either the chlorides or the iodides. This conclusion is not in harmony with the conclusions drawn herein from the experimental data that are considered reliable. The whole treatment is highly speculative and illustrates the great complexity of the problem.

The problem may be simplified to some extent if the combustion of hydrogen is considered instead of methane. The mechanism of the hydrogen-oxygen reaction is fairly well established. It is known that the rate of branching is dependent on the hydrogen-atom concentration. Any compound that would remove hydrogen atoms would

therefore have a profound inhibiting action upon the reaction rate. As previously stated, Hinshelwood has explained the inhibiting action of the halogens on the basis of the reaction



Such a hypothesis is highly plausible. Bodenstein and Jung (reference 51), by use of hydrogen atoms produced in a Wood's tube, showed that such reactions are extremely rapid. Similarly, the inhibiting action of the alkyl halides might be explained by reactions of the type



Chadwell and Titani (reference 52), using the Wood's tube method, investigated the reactions between hydrogen atoms and several of the simpler alkyl halides. Their results are explained on the basis of reactions similar to reaction (12), and indicate that reactivity increases in ascending the series RF, RCl, RBr, RI. Thus, the iodides would be expected to be the best extinguishing agents, in harmony with experimental fact. In addition, the products of dissociation of the alkyl halides, namely X atoms and X₂, would also tend to remove the hydrogen atoms rapidly.

It is known that hydrogen atoms occur in hydrocarbon flames as a result of pyrolysis of the hydrocarbon. The importance of these atoms has recently been emphasized. Tanford and Pease (references 53 to 55) and Badin, Stuart, and Pease (reference 56) showed that the flame speed in carbon monoxide - hydrogen mixtures and in butadiene is a direct function of the hydrogen-atom concentration, but is independent of the concentrations of the other atoms and free radicals. Axford and Norrish (reference 57) have postulated a mechanism for the oxidation of formaldehyde, which occurs as an intermediate in many hydrocarbon oxidations, involving only hydrogen atoms and hydroxyl radicals as the chain carriers. It would therefore appear that any substance that would react with hydrogen atoms could act as an effective inhibitor of hydrocarbon combustions as well as of the hydrogen combustion. The action of inhibitors of hydrocarbon combustions may therefore be interpreted in the same manner as in the hydrogen combustion. This discussion is all speculative and is offered only as a working hypothesis for future investigations.

Relative importance of the different actions. - Some, or possibly all, of the five actions of fire-extinguishing agents are operative during the extinguishing of a fire. Evaluation of their relative importance therefore becomes very complex. The gaseous and liquid extinguishing agents will be considered first; and then the metallic salts.

The mechanical action is primarily a function of the method of application, being dependent on the manner in which the agent strikes across the flame; it is probably of major importance in extinguishing most aircraft fires. The blanketing action is mainly a function of the rate of application but also depends on the volatility and the density of the extinguishing agent. The CAA found that the rate of application is the most important factor affecting the ability of an agent to extinguish fires. From this fact, it would seem that the blanketing action of extinguishing agents is one of the most important actions.

Cooling action is a function of the physical properties of the agent, that is, heat capacity, thermal conductivity, and the heat of vaporization, and will be of different magnitude for different agents. The differences in extinguishing effectiveness of the various "inert" gases (helium, argon, nitrogen, carbon dioxide, and water vapor), as measured in inflammable-limits studies, are adequately explained by differences in cooling action. The cooling action obviously is also a function of the amount of agent employed. With most extinguishing agents, except water and highly compressed carbon dioxide, the amounts used are small and the cooling action is of only secondary importance.

The importance of the chemical actions are indicated by the greatly enhanced extinguishing effectiveness of the gaseous and liquid halogen-containing compounds, as determined in inflammable-limits studies. These compounds have larger specific heats than the inert gases and the cooling action would therefore be increased, but the increase is not large enough to account for the much greater effectiveness of many of the compounds investigated by Jorissen. In addition, there is no relation between extinguishing effectiveness and specific heat among the halogen compounds. This effect therefore must be derived from strong chemical actions.

Although the chemical actions appear much more important than the cooling action, it is difficult to appraise their importance relative to the blanketing and mechanical actions. Such an appraisal could be made from a quantitative correlation between results obtained from inflammable-limits studies, which measure

chemical actions (and cooling action), and those obtained by direct-application methods. The Purdue University investigation attempted such a correlation with several gaseous extinguishing agents. The experiments were previously discussed and the results given in table XIII. It can be seen from this table that, qualitatively, the order of effectiveness is the same for each type of test, but no quantitative conclusions may be drawn because of the uncertainty in the results of the direct-application experiments. A further substantiation may be obtained by comparing the order of effectiveness of the common extinguishing agents obtained from direct-application methods with the results of the Purdue University investigation obtained from inflammable-limits studies of *n*-heptane. These results are represented in table XVIII and also display a correlation. It would therefore appear that the chemical actions are important, but because of lack of quantitative data it is impossible to determine just how important.

For metal salts, the main action appears to be chemical in nature. This fact is self-evident for water solutions because the addition of the salt can hardly produce any marked change in the cooling and blanketing properties of the water. For dusts and powders, there is little blanketing action; Dufraisse and German (reference 9) have shown that the extinguishing effect arises primarily from the undecomposed salt. Muraour and Michel-Lévy (reference 33) have shown that there is little cooling action, which is substantiated by the fact that, for the alkali metal halides, the compounds with the smallest specific heat are the most effective extinguishing agents. The chemical action involved must therefore be a chain-breaking action.

Because of the importance of the hydrogen atom in hydrocarbon combustions, the hypothesis of Willbourn and Hinshelwood (reference 48) for the effect of alkali metal halides on the hydrogen-oxygen reaction offers a simple explanation for the chain-breaking action of these metallic salts.

CONCLUDING REMARKS

On the practical basis of discovering more efficient fire-extinguishing agents, an empirical approach will yield the most immediate results at the present stage of knowledge. From the preceding analysis, it appears that improvements in extinguishing agents may come by the discovery of substances that exhibit strong chemical actions.

The chemical action of different substances can be rated quantitatively by inflammable-limits studies. These measurements are influenced by cooling action and some diluting action, but these actions should be of secondary importance compared with the chemical action. They should not, however, be entirely neglected in the interpretation of the results.

The organic halogen compounds seem to be the most promising class of compounds to investigate. A systematic survey of a large number of these organic halides should be made in an attempt to correlate extinguishing effectiveness with structure and chemical properties. Studies should be made of the change of effectiveness of substances in different homologous series. Different isomeric compounds should be studied to determine the influence of branching, of different types of unsaturation, and of change of bond strength. In addition to the organic halogen compounds, the free halogens and their hydrogen acids should be evaluated; for the effect of the organic halogens may be due merely to the liberation of these compounds, although the results of Dufraisse, Vieillefosse, and Le Bras indicate that this is not the case. An investigation of this type would serve two purposes: (1) From the information obtained, it should be possible to draw empirical rules that would be valuable in selecting compounds for fire-extinguishing agents; and (2) the information should give a better insight into the nature of the chemical actions involved.

Although the chemical actions appear to be important in fire extinguishing, their importance must not be over emphasized. As was previously stated, it is impossible at present to give a quantitative evaluation of the significance of the chemical actions relative to the blanketing and mechanical actions because no reproducible quantitative data on the relative efficiencies of different agents have been obtained by direct-application methods. It is therefore necessary to develop a standard test fire and a standard procedure from which such data may be obtained. A comparison of these results with those obtained from inflammable-limits studies would indicate how large a difference in chemical action is required to produce a noticeable increase in fire-extinguishing effectiveness. Such information is essential.

The CAA is developing a quantitative test procedure for rating different extinguishing agents by a direct-application method. A comparison of some of their preliminary results with those the Purdue University investigation obtained from inflammable-limits studies displays only a fair correlation and indicates that a rather large

difference in chemical action is required to produce a noticeable change in fire-extinguishing efficiency. The influence of experimental conditions on these results has not, however, been fully investigated and no general conclusion should be drawn as yet.

No consideration has been taken of the toxicity of the possible fire-extinguishing substances. Little is known about the toxicity of most of the organic halogen compounds, but it is known that the majority of them will give off toxic vapors when applied to fires. Fortunately, considerable amounts of pungent acid are formed, and these acids give sufficient warning. This objection, which applies at present to methylbromide and carbon tetrachloride, would prohibit the use of these agents in confined, occupied spaces. In aircraft, however, fires in the engines and wings are by far the most prevalent.

On the theoretical basis of elucidating the chemical action of extinguishing agents, the problem is so complex and so far from solution that nearly any approach to it will yield valuable information. Of prime importance, of course, is the solution of the mechanisms of hydrocarbon combustions and the determination of what radicals act as the chain carriers.

At present, only the mechanism of the hydrogen combustion reaction is well understood. Kinetic studies of this reaction in different temperature regions, employing different organic halides as inhibitors, should yield valuable information pertinent to the actions of extinguishing agents. Also, an extension of Le Bras' experiments on the hydrogen flame to other halides in addition to ethylbromide should give significant results.

Spectroscopy has provided a valuable technique for the elucidation of combustion processes, and it should yield valuable information if applied to extinguishing. The effect of different inhibitors on the absorption spectra of different combustibles at elevated temperatures should yield pertinent data, as should the effect of different inhibitors on the emission spectra of flames of different combustibles.

For a final quantitative treatment of extinguishing, it will be necessary to know the energies of activation of the various possible elementary reactions involving the organic halides as the chain carriers in the combustion reactions. Information concerning bond strengths in these compounds will be required, as will information about their dissociation in the region in front

of a flame. Such information is so difficult to obtain, and techniques are so complicated, that the best approach at present would probably be to confine attention to the hydrogen and methane combustions, and to inhibition by some of the simpler alkyl halides or the halogens themselves. For these compounds, some of the necessary facts are already available.

Lewis Flight Propulsion Laboratory,
National Advisory Committee for Aeronautics,
Cleveland, Ohio, September 27, 1949.

REFERENCES

1. Cleveland Laboratory Aircraft Fire Research Panel: Preliminary Survey of the Aircraft Fire Problem. NACA RM ESB18, 1948.
2. Rhead, Thomas Fred Eric: Residual and Extinguishing Atmospheres of Flames. Jour. Soc. Chem. Ind. (London), vol. XXXVII, no. 16, Aug. 31, 1918, pp. 274t-281t.
3. Verbrugh, A. J.: On the Relation between Extinction Limits of Stationary Flames and Ternary Explosion Limits. Rec. trav. chim. (Amsterdam), T. 59, 1940, P. 983-1020.
4. Dufraisse, Charles, Vieillefosse, Roger, et Le Braz, Jean: Applications de l'effet antioxygène au problème de la lutte contre l'incendie. L'extinction des flammes. Comptes Rendus, T. 197, Juillet-Déc. 1933, P. 162-164.
5. Dufraisse, Charles, et Le Braz, Jean: Applications de l'effet antioxygène au problème de la lutte contre l'incendie. L'extinction des flammes. Comptes Rendus, T. 199, Juillet-Déc. 1934, P. 75-78.
6. Dufraisse, Charles, et Le Bras, Jean: Étude sur le mécanisme extincteur du tétrachlorure de carbone envers les flammes. Comptes Rendus, T. 202, Jan.-Juin 1936, P. 227-230.
7. Dufraisse, Charles, et Le Bras, Jean: Les corps combustibles, envisagés comme adjuvants des extincteurs incombustibles, pour l'extinction pratique des flammes. Comptes Rendus, T. 205, Juillet-Déc. 1937, P. 562-565.

8. Le Bras, Jean: Recherches sur l'extinction des flammes. Rec. trav. chim. (Amsterdam), T. 61, 1942, P. 425-444.
9. Dufraisse, Charles, et German, Manuel: Étude sur le mécanisme de l'extinction sèche par les poussières. Nitrate, chlorate, perchlorate de potassium et autres corps comburants comme extincteurs des flammes. Comptes Rendus, T. 207, Juillet-Déc. 1938, P. 1221-1225.
10. Davy, Humphrey: Some Researches on Flame. Phil. Trans. Roy. Soc. London, pt. I, 1817, pp. 45-76.
11. Jorissen, W. P., and Velisek, J.: On the Influence of Some Noninflammable Vapours of Organic Liquids on the Limits of Inflammability of Methane Air Mixtures. Rec. trav. chim. (Amsterdam), T. XLIII, 1924, P. 80-86.
12. Anon.: Short review of various aspects of Jorissen's work. Chem. Weekblad, Jaarg. 18, Nr. 45, Nov. 5, 1921, S. 636.
13. Jorissen, W. P., and Meuwissen, J. C.: On the Influence of Some Noninflammable Vapours of Organic Liquids on the Limits of Inflammability of Methane Air Mixtures, II. Rec. trav. chim. (Amsterdam), T. XLIII, 1924, P. 591-597.
14. Jorissen, W. P., and Meuwissen, J. C.: The Influence of Some Noninflammable Vapours of Organic Liquids on the Limits of Inflammability of Mixtures of Inflammable Gases and Air - III. Rec. trav. chim. (Amsterdam), T. XLIV, 1925, P. 132-140.
15. Jorissen, W. P., and van der Valk, J. H. A. P. Langen: The Influence of Dichloro- and Trichloroethylene on the Limits of Inflammability of Carbon Monoxide-Air Mixtures. Rec. trav. chim. (Amsterdam), T. XLIV, 1925, P. 810-813.
16. Jorissen, W. P.: Explosive Reactions and Negative Catalysts. Collection of Czechoslovak Chemical Communications (Prague), 1930, pp. 288-291.
17. Jorissen, W. P., Booy, J., and van Heiningen, J.: Reaction-Regions, XXII. On the Prevention of Explosive Reactions in Gas and Vapour Mixture by Small Amounts of Various Substances. Rec. trav. chim. (Amsterdam), T. LI, 1932, P. 868-877.

18. Jorissen, W. P., and Hermans, J. J.: Reaction-Regions, XXIII. On the Prevention of Explosive Reactions in Gas and Vapour Mixtures by Small Amounts of Various Substances. II. Rec. trav. chim. (Amsterdam), T. LIII, 1933, P. 271-274.
19. Coward, Hubert Frank, and Hartwell, Francis John: Extinction of Methane Flames by Diluent Gases. Jour. Chem. Soc. (London), pt. I, 1926, pp. 1522-1532.
20. Coward, Hubert Frank, and Brinsley, Frank: The Dilution-limits of Inflammability of Gaseous Mixtures. Part I. The Determination of Dilution-limits. II. The Lower Limits for Hydrogen, Methane and Carbon Monoxide in Air. Jour. Chem. Soc. (London), vol. CV, pt. II, 1941, pp. 1859-1885.
21. Coward, H. F., and Jones, G. W.: Extinction of Methane-Air Flames by Some Chlorinated Hydrocarbons. Ind. and Eng. Chem. (Ind. ed.), vol. 18, no. 9, Sept. 1926, pp. 970-974.
22. Jones, G. W., and Perrott, G. St. J.: Extinction of Methane Flames by Dichloro-Difluoro-Methane. R.I. 3042, Bur. Mines, Oct. 1930.
23. Coward, Hubert Frank, and Gleadall, John Jebson: Extinction of Methyl Flames by Water Vapour. Jour. Chem. Soc. (London), pt. I, 1930, pp. 243-248.
24. Jones, G. W., and Scott, F. E.: Extinction of Propane and Butane Flames by Dichlorodifluoromethane. R.I. 3908, Bur. Mines, 1946.
25. Jones, G. W., and Kennedy, R. E.: Inflammability of Natural Gas: Effect of Pressure upon the Limits. R.I. 3798, Bur. Mines, Feb. 1945.
26. Payman, W.: Researches on Coal-Mining Explosives at the Safety in Mines Research Station, Buxton. Trans. Inst. Mining Eng. (London), vol. LXXX, 1930-1931, pp. 11-19; discussion, pp. 19-23.

27. Naylor, Clement Albert, and Wheeler, Richard Vernon: The Ignition of Gases. Part VI. Ignition by a Heated Surface. Mixtures of Methane with Oxygen and Nitrogen, Argon, or Helium. Jour. Chem. Soc. (London), pt. II, 1931, pp. 2456-2467.
28. Coward, H. F.: Ignition Temperatures of Gases. "Concentric Tube" Experiments of (the late) Harold Daily Dixon. Jour. Chem. Soc. (London), pt. II, July-Dec. 1934, pp. 1382-1406.
29. Prettre: Action des Halogénures alcalins sur les températures d'auto-inflammation des mélanges d'oxyde de carbone et d'air. Mémorial des Poudres (Paris), T. 25, 1932-1933, P. 160-168.
30. Jorissen, W. P., van der Dussen, A. A., Matla, W. P. M., and de Liefde, J. H.: Reaction-Regions, XXV. Systems of Two Gaseous Substances and One Solid Substance. Systems of Two Solid Substances and One Gaseous Substance. Rec. trav. chim. (Amsterdam), T. LIII, 1933, P. 403-412.
31. Dijkman, A. J.: De verhinderig von gasexplosies door vaste stoffen in poederovorm. Chem. Weekblad, Jaar. 31 (No. 48), Nr. 1627, Dec. 1, 1934, S. 718-720.
32. Jorissen, W. P., and Snijders, H. G., and Vink, H. J.: A New Method for the Comparison of the Extinguishing Action of Various Finely-Divided Solid Substances on Explosive Gas Mixtures. Rec. trav. chim. (Amsterdam), T. 59, 1940, P. 957-962.
33. Muraour, Henri, et Michel-Lévy, Albert: Étude de l'influence de différents sels sur l'inflammation, a l'air, de mélanges gazeux combustibles. Comptes Rendus, T. 218, 1944, P. 551-553.
34. Jorissen, W. P.: Sur l'influence de circonstances diverses sur l'étendue et la forme des régions d'explosion. Rec. trav. chim. (Amsterdam), T. 61, 1942, P. 445-451.
35. Dallas, A. W., and Hansberry, H. L.: Determination of Means to Safeguard Aircraft from Powerplant Fires in Flight. Part I. Tech. Development Rep. No. 33, CAA, Sept. 1943.
36. Anon.: Chlorobromomethane. NFPA Quarterly, vol. 42, no. 1, July 1948, pp. 46-50.

37. Williams, Ralph B.: Monochlorbrommethane Demonstration. Memo. Rep. Serial No. TSEPE-651-23, Eng. Div., Air Tech. Service Command, Army Air Forces, Feb. 4, 1946.
38. Ellis, Oliver C. de C.: Extinction of Petrol Fires by Methyl Iodide. *Nature*, vol. 161, no. 4089, March 13, 1948, pp. 402-403.
39. Thomas, Charles Allen, and Hochwalt, Carroll A.: Effect of Alkali-Metal Compounds on Combustion. *Ind. and Eng. Chem.*, vol. 20, no. 6, June 1928, pp. 575-577.
40. Rakuzin, M. A.: Extinguishing Burning Mineral Oils. *Chem. Abs.*, vol. 23, no. 9, May 1929, p. 2282. (Abs. from *Petroleum Zeitschr.*, vol. 24, 1928, pp. 1091-1092.)
41. Garstang, W. L., and Hinshelwood, C. N.: The Kinetics of the Combination of Hydrogen and Oxygen: the Influence of Iodine. *Proc. Roy. Soc. London*, vol. 130, no. 814, ser. A, March 2, 1931, pp. 640-654.
42. Hinshelwood, C. N., and Williamson, A. T.: *The Reaction between Hydrogen and Oxygen*. Clarendon Press (Oxford), 1934.
43. Hadman, G., Thompson, H. W., and Hinshelwood, C. N.: The Oxidation of Carbon Monoxide. *Proc. Roy. Soc. London*, vol. 137, no. A381, ser. A, July 1, 1932, pp. 87-101.
44. Hadman, G., Thompson, H. W., and Hinshelwood, C. N.: The Explosive Oxidation of Carbon Monoxide at Lower Pressures. *Proc. Roy. Soc. London*, vol. 138, no. A835, ser. A, Nov. 1932, pp. 297-311.
45. Norrish, R. G. W., and Foord, S. G.: The Kinetics of the Combustion of Methane. *Proc. Roy. Soc. London*, vol. 157, no. A892, ser. A, Dec. 2, 1936, pp. 503-525.
46. Pease, Robert N.: Characteristics of the Non-Explosive Oxidation of Propane and the Butanes. *Jour. Am. Chem. Soc.*, vol. LI, Jan.-June 1929, pp. 1839-1856.
47. Jorissen, W. P., and Lebbink, H.: On the Influence of Certain Salts on the Lowest Temperature at Which a Reaction between Methane and Oxygen is Observed. *Rec. trav. chim. (Amsterdam)*, T. 58, 1939, P. 959-963.

48. Willbourn, A. H., and Hinshelwood, C. N.: The Mechanism of the Hydrogen-Oxygen Reaction. III. The Influence of Salts. Proc. Roy. Soc. London, vol. 185, no. A1003, ser: A, April 5, 1946, pp. 376-380.
49. Townend, D. T. A., Cohen, L. L., and Mandlekar, M. R.: The Influence of Pressure on the Spontaneous Ignition of Inflammable Gas-Air Mixtures. III - Hexane- and Isobutane-Air Mixtures. Proc. Roy. Soc. London, vol. 146, no. A856, ser. A, Aug. 1, 1934, pp. 113-129.
50. Schaad, Raymond E., and Boord, Cecil E.: Effects of Knock-Suppressing and Knock-Inducing Substances on the Ignition and Partial Combustion of Certain Fuels. Ind. and Eng. Chem. (Ind. ed.), vol. 21, no. 8, Aug. 1929, pp. 756-762.
51. Bodenstein, Max, und Jung, Gerhard: Die Dissoziation der Wasserstoffmolekel. Zeitschr. Phys. Chem., Bd. 121, Heft 1 und 2, Mai 24, 1926, S. 127-135.
52. Chadwell, H. Marshall, and Titani, Toshizo: The Reactions of Atomic Hydrogen with Several Alkyl Halides. Jour. Am. Chem. Soc., vol. 55, no. 4, April 1933, pp. 1363-1376.
53. Tanford, Charles, and Pease, Robert N.: Equilibrium Atom and Free Radical Concentrations in Carbon Monoxide Flames and Correlation with Burning Velocities. Jour. Chem. Phys., vol. 15, no. 7, July 1947, pp. 431-433.
54. Tanford, Charles: Theory of Burning Velocity. I. Temperature and Free Radical Concentrations near the Flame Front, Relative Importance of Heat Conduction and Diffusion. Jour. Chem. Phys., vol. 15, no. 7, July 1947, pp. 433-439.
55. Tanford, Charles, and Pease, Robert N.: Theory of Burning Velocity. II. The Square Root Law for Burning Velocity. Jour. Chem. Phys., vol. 15, no. 12, Dec. 1947, pp. 861-865.
56. Badin, Elmer J., Stuart, Joseph G., and Pease, Robert N.: Burning Velocities of Butadiene-1,3 with Nitrogen-Oxygen and Helium-Oxygen Mixtures. Jour. Chem. Phys., vol. 17, no. 3, March 1949, pp. 314-316.
57. Axford, D. W. E., and Norrish, R. G. W.: The Oxidation of Gaseous Formaldehyde. Proc. Roy. Soc. London, vol. 192, no. 1031, ser. A, March 18, 1949, pp. 518-537.

TABLE I - EXTINCTION CONCENTRATION OF
VARIOUS SUBSTANCES FOR FLAME OF
ILLUMINATING GAS BURNING IN AIR^a

Extinguishing substance	Amount added to air stream (percent by volume)
N ₂	55
CO ₂	40
CH ₃ Cl	20
CH ₂ ClCH ₂ Cl	16
CCl ₄	16
CHCl=CHCl	13
CHCl=CCl ₂	13
CCl ₂ =CCl ₂	13
C ₂ H ₅ Cl	13
CH ₃ Br	10
CCl ₃ CHCl ₂	10
C ₆ H ₅ Cl	10
C ₆ H ₅ Br	9
CH ₃ CH ₂ CH ₂ Cl	8
CH ₃ CHClCH ₃	8
CH ₃ I	7
CHCl ₂ CHCl ₂	7
C ₂ H ₅ Br	7
CH ₂ Br ₂	7
CH ₂ =CHCH ₂ Br	7
CH ₃ C ₆ H ₄ Br (p)	7
(CH ₃) ₂ (CH ₃ ·CH ₂)≡CCl	6
(CH ₃) ₃ ≡CCl	6
CH ₃ (CH ₂) ₂ CH ₂ I	6
CH ₃ CH ₂ CH ₂ Br	6
CH ₃ CHBrCH ₃	6
CH ₂ BrCH ₂ Br	6
C ₂ H ₅ I	5
(CH ₃) ₂ CHCH ₂ CH ₂ Br	5
CH ₃ CHICH ₃	5
CH ₂ I ₂	2.5
HCl	40
HBr	20
HI	10
Cl ₂	50
Br ₂	10
I ₂	2



^aFrom reference 4.

TABLE II - EXTINGUISHING PERCENTAGE OF NITROGEN, CARBON TETRACHLORIDE, AND ETHYLBROMIDE FOR FLAMES OF VARIOUS COMBUSTIBLES^a

Combustible	Velocity of flow of combustible		N ₂			CCl ₄		C ₂ H ₅ Br	
			Amount for extinction (percent by volume)	Minimum oxygen (percent by volume)	Residual oxygen (percent by volume)	Amount for extinction (percent by volume)	Residual oxygen (percent by volume)	Amount for extinction (percent by volume)	Residual oxygen (percent by volume)
H ₂	50	lb/hr	75	5.2	3	70	16	8	2
CO	16	lb/hr	53	9.8	8.1	2.8	19.3	6	2.6
CH ₄	12	lb/hr	35	13.6	8.3	8.5	13.7	5.6	.8
Illuminating gas	30	lb/hr	60	8.4	5.8	26.5	15	6.4	1.8
C ₆ H ₆	30	gm/hr	31.2	14.5	13.3	5.5	13.8	6.2	2
C ₆ H ₅ CH ₃	22	gm/hr	21.8	16.4	15	3	18.6	6	2.4
CH ₃ C ₆ H ₄ OH	18	gm/hr	17	17.6	16	2.6	17.5	5.8	2.6
CH ₃ OH	15.6	gm/hr	33.8	13.9	13.6	11.2	18.3	5.9	4
CH ₃ CH ₂ OH	12.3	gm/hr	26.2	15.5	13.8	8	19	5.7	3.6
CH ₃ (OH) ₂ OH	14	gm/hr	27.4	15.2	13.8	6	16.3	5.2	4.2
CH ₃ (CH ₂) ₃ OH	15.2	gm/hr	28.5	15	13.4	5.8	15.2	5.1	3.6
CS ₂	42	gm/hr	55	9.5	13.8	4	18.6	4	1.6

^aFrom reference 8.



TABLE III - EXTINGUISHIVE EFFECT OF POWDERS ON FLAMES OF HYDROGEN, ILLUMINATING GAS, METHANE, AND CARBON MONOXIDE^a

Powdered extinguishing substance tested	Decomposition data		Minimum dose for extinction (mg/liter) ^b			
	Temperature (°C)	Products	H ₂	Illuminating gas	CH ₄	CO
NaHCO ₃	100	Na ₂ CO ₃ , H ₂ O, CO ₂	700	450	100	300
KHCO ₃	170	K ₂ CO ₃ , H ₂ O, CO ₂	250	100	---	30
KClO ₃	350	KCl, O ₂	++ ^d	++	50	5
NaClO ₃	370	NaCl, O ₂	++	++	150	50
KClO ₄	400	KCl, O ₂	++	++	80	30
KNO ₃	500	NO ₂	450	100	15	8
NaN ₃	480	NO ₂	550	250	50	40
Talc	1000	-----	>800	>800	>800	>800
Na ₂ B ₄ O ₇ ·10H ₂ O	50	Na ₂ B ₄ O ₇ ·2H ₂ O, 8H ₂ O	>600	300	150	+
Na ₂ SO ₄ ·10H ₂ O	20	Na ₂ SO ₄ , 10H ₂ O	>800	>800	200	+
Na ₂ SO ₄	1200	-----	>600	>600	600	500



^aFrom reference 9.

^bFigures given correspond approximately to concentration in mg/liter calculated for uniform distribution.

^cCarbon monoxide used had constant water content very little below saturation value at 20°, which is 2.24 percent.

^dThe signs ++ and + indicate that the flame is more or less enlivened. The sign > indicates that the flame seemed impeded without being extinguished by the largest quantity of powder that could be used in the apparatus.

TABLE IV - RESULTS OF JORISSEN ON INFLUENCE OF
ADDITIVES ON INFLAMMABLE REGION OF METHANE-AIR
MIXTURES AT ROOM TEMPERATURE^a

Extinguishing substance	Amount required to render noninflammable all CH ₄ -air mixtures (percent by volume)	Reference
POCl ₃	1	17
(CH ₃) ₂ CH ₂ CH ₂ CH ₂ Br	1.5	18
CH ₃ CH ₂ I	5.3	17
SiCl ₄	5.6	17
SO ₂ Cl ₂	7.0	17
CH ₃ CH ₂ CH ₂ Br	7.6	17
CCl ₄	7.8	13
SiHCl ₃	8.0	17
CO ₂	21.2	16
He	26	16
N ₂	30.8	16
(CH ₃) ₃ CCl	Flammable	16, 17


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^aLimits of explosion of CH₄ in air were approximately 6 and 14 percent CH₄ by volume.

TABLE V - RESULTS OF BUREAU OF MINES AND SAFETY IN MINES RESEARCH BOARD ON INFLUENCE OF ADDITIVES ON INFLAMMABLE REGION OF METHANE-AIR MIXTURES AT ROOM TEMPERATURE^a

Extinguishing substance	Amount required to render noninflammable all CH ₄ -air mixtures (percent by volume)	Reference
CCl ₂ F ₂	11.5	22, 24
CCl ₄	12.2, 11.5	21, 22
CO ₂	25	19
H ₂ O	^b 29.1	23
N ₂	38	19
He	38.5	19
A	51	19
C ₂ H ₂ Cl ₂	Inflammable	21



^aInflammable limits of CH₄ in air were 5.0- and 15.0-percent CH₄ by volume.

^bTaken at 67° C. Value for CO₂ at this temperature was 27.1 percent.

TABLE VI - RESULTS OF BUREAU OF MINES ON INFLUENCE OF ADDITIVES ON INFLAMMABLE REGIONS OF COMBUSTIBLE GASES IN AIR AT ROOM TEMPERATURE AND ATMOSPHERIC PRESSURE^a

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Combustible	Volumes of added gas required to render noninflammable one volume of combustible gas under all conditions				
	N ₂	CO ₂	CCl ₄	CCl ₂ F ₂	CO ₂ /N ₂
H ₂	16.5	10.2	----	-----	0.62
CO	4.1	2.2	----	-----	.54
CH ₄	6.0	3.3	1.4	1.4	.55
C ₂ H ₆	12.8	7.3	----	-----	.57
C ₃ H ₈	14.9	7.9	----	2.8	.53
C ₄ H ₁₀	17.2	9.3	----	3.2	.54
C ₅ H ₁₂	22.3	12.2	----	-----	.55
C ₆ H ₁₄	25.0	14.0	----	-----	.56
Gasoline	24.2	14.2	----	3.9	.59
C ₂ H ₄	15.3	9.0	----	-----	.59
C ₃ H ₆	14.0	7.7	----	-----	.55
CH ₂ =CHCH=CH ₂	19.6	12.0	----	-----	.61
$\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ \diagdown \quad \diagup \\ \text{CH}_2 \end{array}$	13.5	8.0	----	-----	.59
C ₆ H ₆	21.2	12.9	----	-----	.61
Average					0.57



^aFrom reference 24.

TABLE VII - INFLUENCE OF ADDITIVES OF INFLAMMABLE REGION OF n-HEPTANE-AIR MIXTURES^a

Extinguishing substance	Amount required to render noninflammable all heptane-air mixtures (percent by volume)	Extinguishing substance	Amount required to render noninflammable all CH ₄ -air mixtures (percent by volume)
CF ₃ CHBrCH ₃	4.9	CF ₃ CHClCH ₃	12.0
CBrF ₂ CBrF ₂	4.9	CF ₃ CH ₂ CH ₂ Cl	12.2
CH ₂ Br ₂	5.2	CClF ₃	12.3
CF ₃ CH ₂ CH ₂ Br	5.4	C ₂ F ₆	13.4
CH ₃ I	6.1	CCl ₂ F ₂	14.9
CBrF ₃	6.1	CHF ₃	17.8
CClF ₂ CHBrCH ₃	6.4	CHClF ₂	17.9
CF ₃ CH ₂ Br	6.8	SF ₆	20.5
C ₂ F ₁₁ C ₂ F ₅	6.8	CF ₄	26
1,3-C ₆ F ₁₀ (CF ₃) ₂	6.8	CO ₂	29.5
1,4-C ₆ F ₁₀ (CF ₃) ₂	6.8	CH ₂ Cl ₂	Inflammable
CH ₂ BrCH ₂ Cl	7.2	C ₆ H ₄ (CF ₃) ₂	Do.
C ₆ F ₁₁ CF ₃	7.5	C ₆ H ₅ CF ₃	Do.
C ₇ F ₁₆	7.5	NF ₃	Explosive
CH ₂ BrCl	7.6	C ₂ F ₄	Inflammable
CClF ₂ CCl ₂ F	9.0		
CH ₃ Br	9.7		
C ₄ F ₁₀	9.8		
CCl ₄	11.5		


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^aFrom Purdue University investigation.

TABLE VIII - EFFECT OF 'INHIBITORS' ON THE IGNITION TEMPERATURE OF 5.8-PERCENT METHANE-AIR MIXTURE^a

Substance	Ignition temperature (°C)	Lag (sec)
I ₂ , 0.2 percent	749	3.6
CH ₃ CH ₂ I, 0.03 percent	760	2.8
CH ₃ CH ₂ Br, 0.24 percent	744	3.6
CCl ₄ , 0.23 percent	689	3.0
Pb(C ₂ H ₅) ₄ , trace	707	55.0
No addition	632	18.5

^aFrom reference 27.

TABLE IX - EFFECT OF PHOSPHORYL CHLORIDE ON MEAN FLAME SPEED OF METHANE-AIR MIXTURES^a

Mixture		Mean flame speed (cm/sec)
Amount CH ₄ (percent by volume)	Amount POCl ₃ (percent by volume)	
9.97	0	92.5
9.84	1.33	-----
9.83	1.38	31
9.73	2.97	30
9.7	3.0	28
9.6	3.9	31



^aFrom reference 34.

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TABLE X - FIRE-EXTINGUISHING AGENTS FOR USE IN TYPE OF AIRCRAFT
POWER-PLANT INSTALLATION TESTED^a

Order of merit	Power section (oil fires)	Accessory section		Over all (b)
		Oil fires with source in power section	Gasoline fires shut off before extinction	
1	CH ₃ Br Mixture (A)	CH ₃ Br Mixture (A)	CH ₃ Br	CH ₃ Br
2	CO ₂ CCl ₄ Mixture (C)	CO ₂ CCl ₄ NaHCO ₃ Mixture (C)	CO ₂	CO ₂
3	NaHCO ₃	K ₂ CO ₃ Mixture (B)	CCl ₄ Mixture (A) Mixture (C)	CCl ₄ Mixture (C) Mixture (A)
4	K ₂ CO ₃ Mixture (B)		K ₂ CO ₃	Na ₂ CO ₃
5				K ₂ CO ₃ Mixture (B)

Mixture (A) indicates a mixture of 30-percent methylbromide and 70-percent carbon tetrachloride.

Mixture (B) indicates a mixture of 30-percent methylbromide and 70-percent methylenechloride.

Mixture (C) indicates various mixture of carbon dioxide and carbon tetrachloride.

^aFrom reference 35.

^bOnly methylbromide and carbon dioxide are considered satisfactory for general use in type of engine installation tested.



TABLE XI - NECESSARY MINIMUM QUANTITIES OF
EXTINGUISHING AGENTS DETERMINED BY TESTS
BASED ON DURATION OF 2 SECONDS^a

	CO ₂	CH ₃ Br		Other liquids (qt) ^b
	(lb)	(lb)	(qt)	
Power section	14.0	10.8	3.0	3.4
Accessory section	5.8	4.4	1.2	1.6
Oil cooler	.6	1.4	.4	.4
Exhaust stack	1.2	1.4	.4	.6
Total	21.6	18.0	5.0	6.0

^aFrom reference 35.

^bOther liquids include: Carbon tetrachloride, mixture of 70-percent carbon tetrachloride and 30-percent methylbromide, and mixtures of carbon dioxide and carbon tetrachloride.

TABLE XII - QUANTITIES OF EXTINGUISHING AGENTS REQUIRED TO PUT OUT STANDARD TEST FIRE^a

Amount of gasoline (cc)	Time of burning (sec)	Type of extinguisher	Amount and type of agent	Time for extinction
200	20	Wash bottle	18 cc CH ₂ ClBr	1 sec
200	20	Wash bottle	200 cc CCl ₄	Not extinguished
200	20	1 qt std.	Pyrene (?cc)	9 sec
400	30	1 qt std.	CH ₂ ClBr (?cc)	1.5 sec
400	30	1 qt std.	1 qt CCl ₄	Not extinguished
400	30	1 qt std.	1 qt Pyrene	Not extinguished

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^aFrom reference 37.

TABLE XIII - RESULTS OF TESTS TO CORRELATE EFFECTIVENESS
IN DECREASING LIMITS OF INFLAMMABILITY OF n-HEPTANE
IN AIR AND EFFECTIVENESS IN EXTINGUISHING A
SMALL TEST FIRE OF n-HEPTANE^a

Gaseous substances tested	Volume necessary to extinguish test fire, (ml)	Amount required to make inflammability limits coincide (percent by volume)
CBrF_3	34	6.1
CClF_3	52	12.3
CH_3Br	52	9.7
CCl_2F_2	61	14.9
CO_2	125	29.5

The NACA logo is a stylized wing shape with the letters "NACA" inside.

^aFrom Purdue University investigation.

TABLE XIV - FIRE-EXTINGUISHING EFFECTIVENESS OF COM-
POUNDS OF ALKALI METALS IN WATER SOLUTION^a

Compound	Concentration of solution (smallest effective normality)	Effect in extinguishing fire
Cesium Chloride	0.8	Positive
Rubidium Bitartrate	.15	Do.
Chloride	1.0	Do.
Carbonate	1.5	Do.
Potassium Bitartrate	.15	Do.
Dichromate	.2	Do.
Perchlorate	.2	Do.
Anthranilate	.25	Do.
Permanganate	.3	Do.
Iodate	.3	Do.
Gallate	.3	Do.
Butyrate	.4	Do.
Citrate	.4	Do.
Lactate	.6	Do.
Hydroxide	.6	Do.
Chlorate	.6	Do.
Iodide	.6	Do.
Fluoride	.6	Do.
Acetate	.7	Do.
Bicarbonate	.7	Do.
Formate	.8	Do.
Tartrate	.8	Do.
Nitrite	.9	Do.
Chloride	1.0	Do.
Nitrate	1.1	Do.
Oxalate	1.1	Do.
Carbonate	1.5	Do.
Bromate	1.5	Do.
Bromide	1.85	Do.
Sodium carbonate	2.5	Do.
Phosphate	4.0	Do.
Hydrogen sulfate	10.0	Negative
Sodium Acetate	1.0	Positive
Dichromate	2.0	Do.
Potassium carbonate	2.5	Do.
Nitrate	3.0	Do.
Lactate	3.5	Do.
Chloride	4.7	Do.
Tartrate	6.0	Negative
Phosphate (di and tri)	Saturated solution	Do.
Lithium Acetate	5.0	Positive
Citrate	6.0	Negative
Nitrate	10.0	Do.
Chloride	15.0	Do.

^aFrom reference 39.



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TABLE XV - COMPARATIVE EFFECT OF ALKALI METALS WITH INCREASE IN ATOMIC WEIGHT^a

Radical	Li	Na	K	Ru	Cs
Cl	^b 15.0	4.7	1.0	1.0	0.8
CH ₃ CO ₂	5.0	1.0	.7	-----	-----
HC ₄ H ₄ O ₆	-----	-----	.15	.15	-----
NO ₃	^b 10.0	3.0	1.10	-----	-----
CO ₃	-----	-----	1.50	1.50	-----

^aFrom reference 39.

^bNo effect on fire (limit of solubility).

TABLE XVI - EFFECT OF POTASSIUM HALIDES WITH AND WITHOUT COMBINED OXYGEN^a

Compound	Smallest effective normality	Compound	Smallest effective normality	Compound	Smallest effective normality
KI	0.6	KIO ₃	0.3	-----	-----
KF	.6	-----	-----	-----	-----
KCl	1.0	KClO ₃	.6	KClO ₄	0.2
KBr	1.85	KBrO ₃	1.5	-----	-----



^aFrom reference 39.

TABLE XVII - INFLUENCE OF SALTS ON FIRST EX-
PLOSION LIMIT OF THE HYDROGEN-OXYGEN
REACTION^a

Nature of surface	Pressure of first limit (mm)	Relative values of the limit
Silica	0.5	1
KF	6.6	13
KCl	3.5	7
KBr	5.0	10
KI	8.5	17
KCl/KI (1:1)	9.0	18
CsCl	4.0	8
CsI	8.6	17
CaCl ₂	1.2	2.4
BaCl ₂	1.3	2.6
K ₂ SO ₄	5.2	10.4



^aFrom reference 48.

TABLE XVIII - CORRELATION BETWEEN RESULTS OBTAINED BY DIRECT APPLICATION TO TEST FIRES AND THOSE OBTAINED BY McBEE AND WELCH^a IN EFFECT OF DECREASING LIMITS OF INFLAMMABILITY OF HEPTANE IN AIR

Extinguishing substance	Amount required to render noninflammable (percent by volume)
CH ₃ I	6.1
CH ₂ BrCl	7.6
CH ₃ Br	9.7
CCl ₄	11.5
CO ₂	29.5



^aFrom Purdue University investigation.

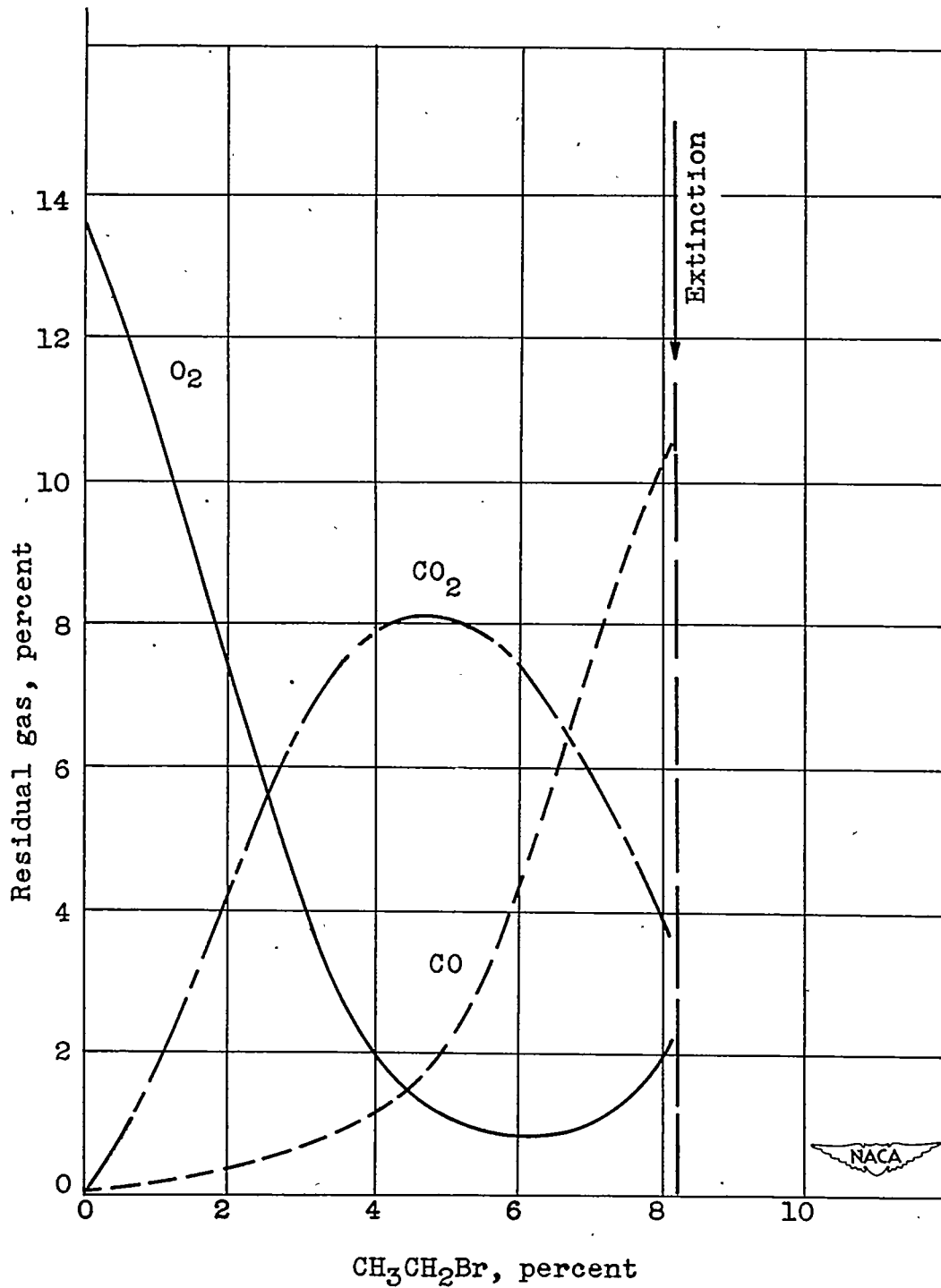


Figure 1. - Variation of percentages of oxygen, carbon-dioxide, and carbon monoxide in residual gases (dried and HBr removed) of flame of hydrogen at 50 liters per hour fed by air containing ethylbromide (reference 8).

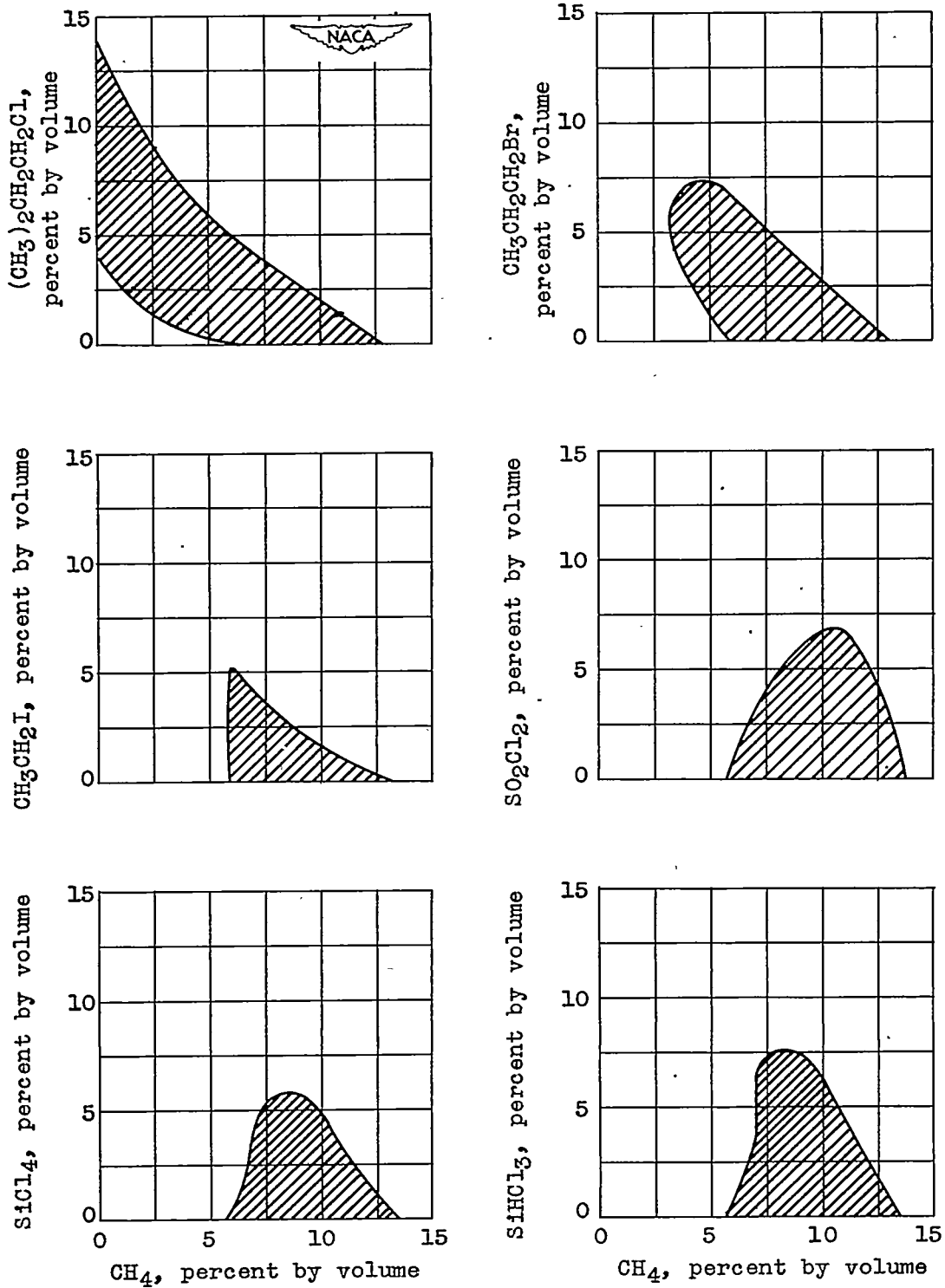


Figure 2. - Inflammable regions for methane in air containing different halides (reference 17). Hatched areas are regions of inflammability.

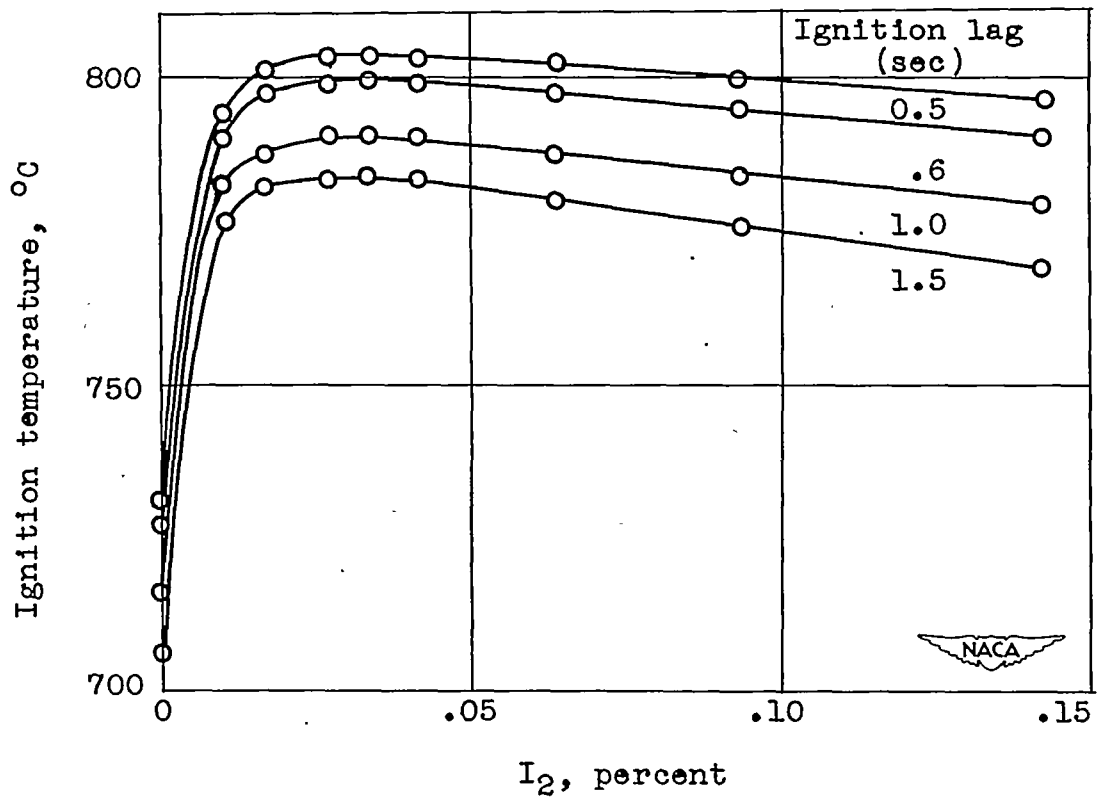


Figure 3. - Ignition points of methane in air containing free iodine (reference 28).

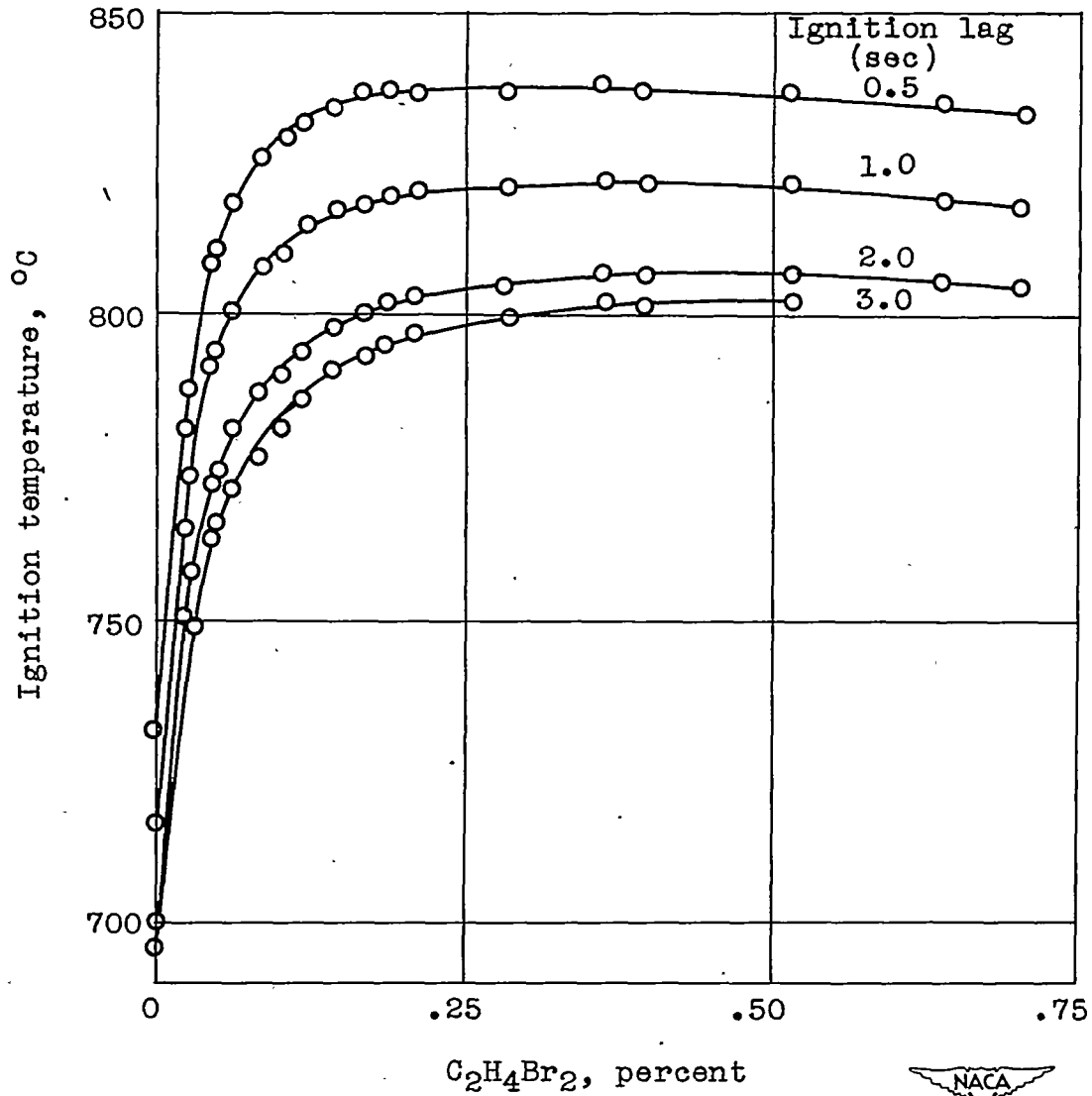


Figure 4. - Ignition points of methane in air containing ethylenebromide (reference 28).

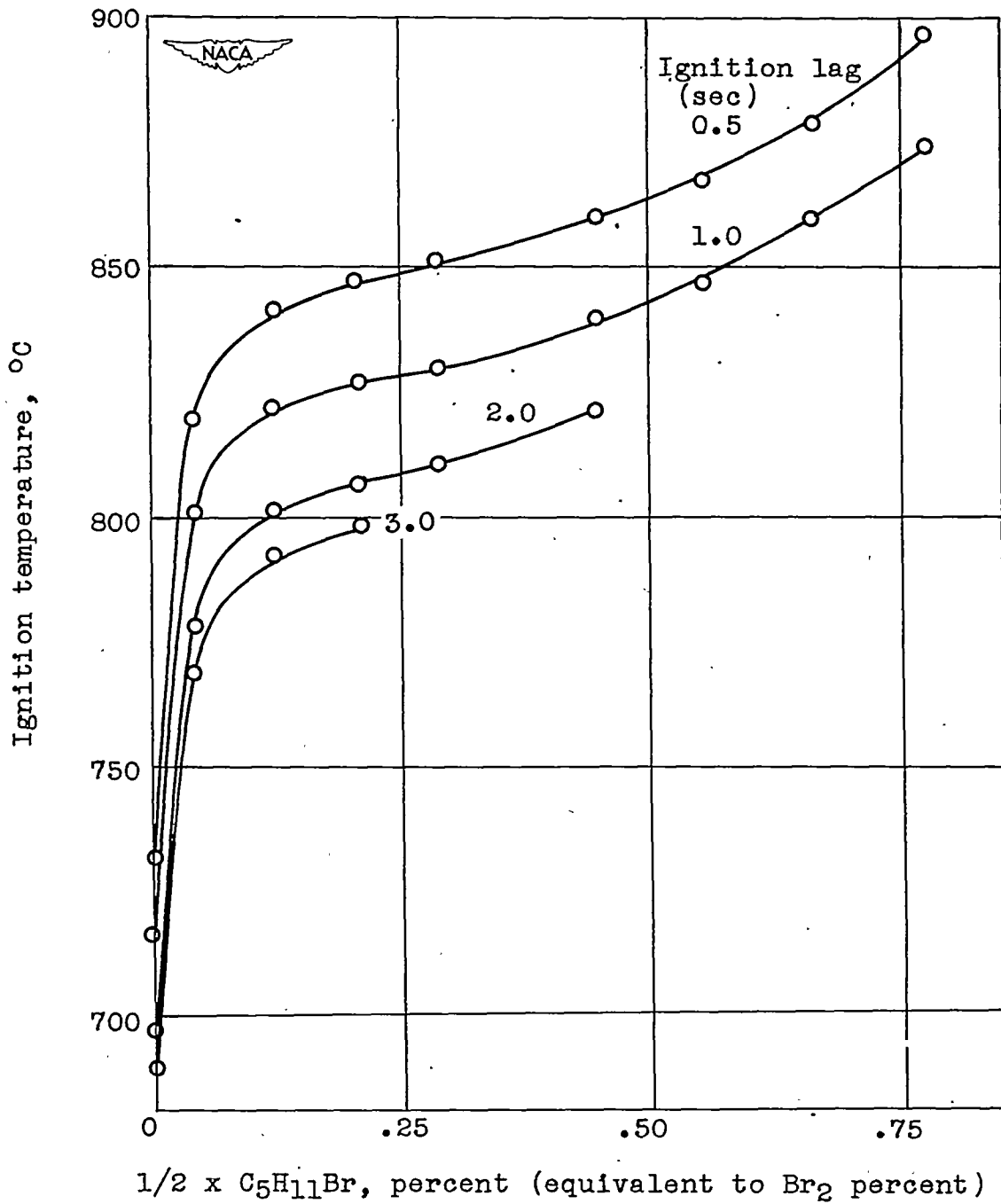


Figure 5. - Ignition points of methane in air containing isoamylbromide (reference 28).

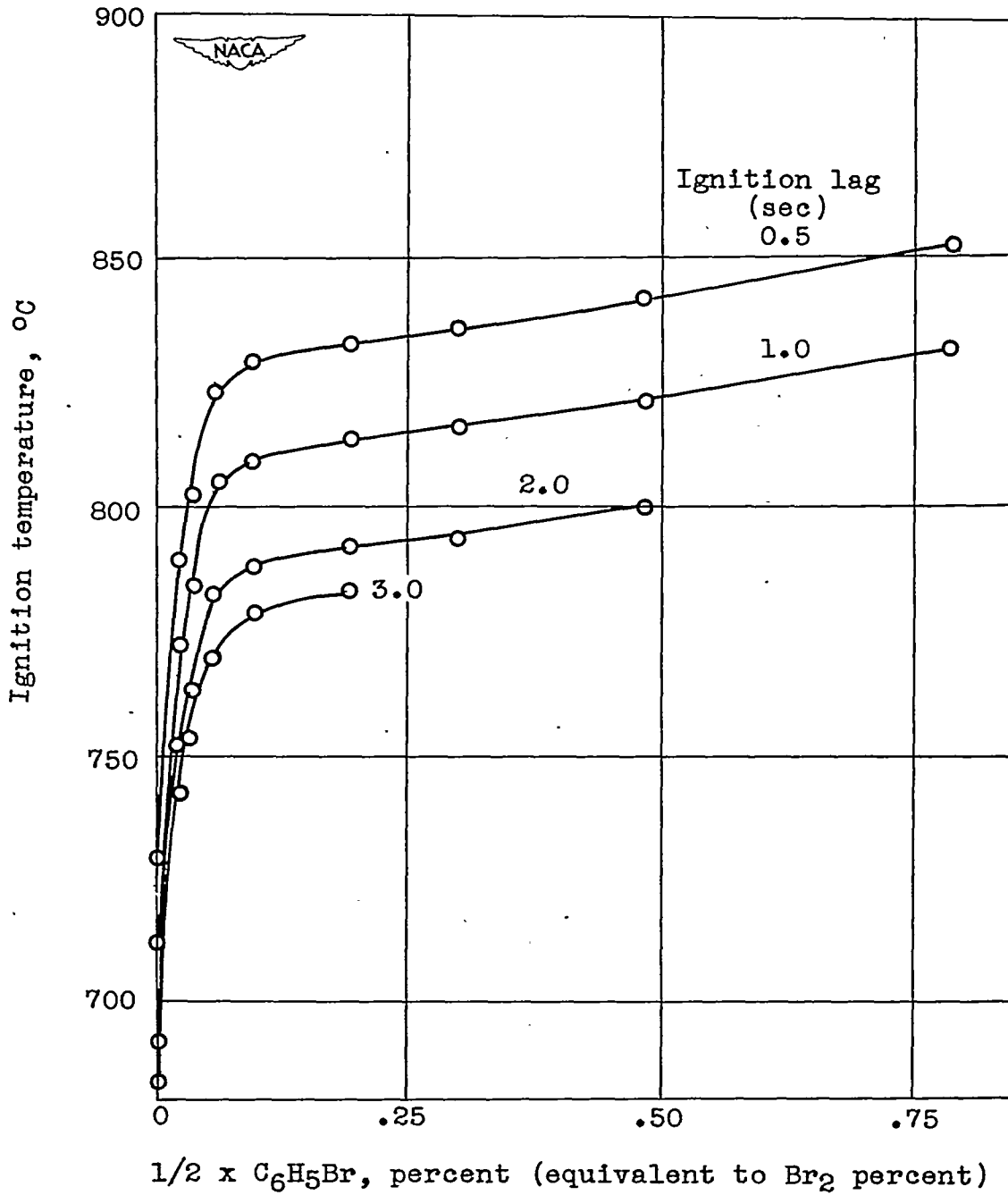


Figure 6. - Ignition points of methane in air containing bromobenzene (reference 28).

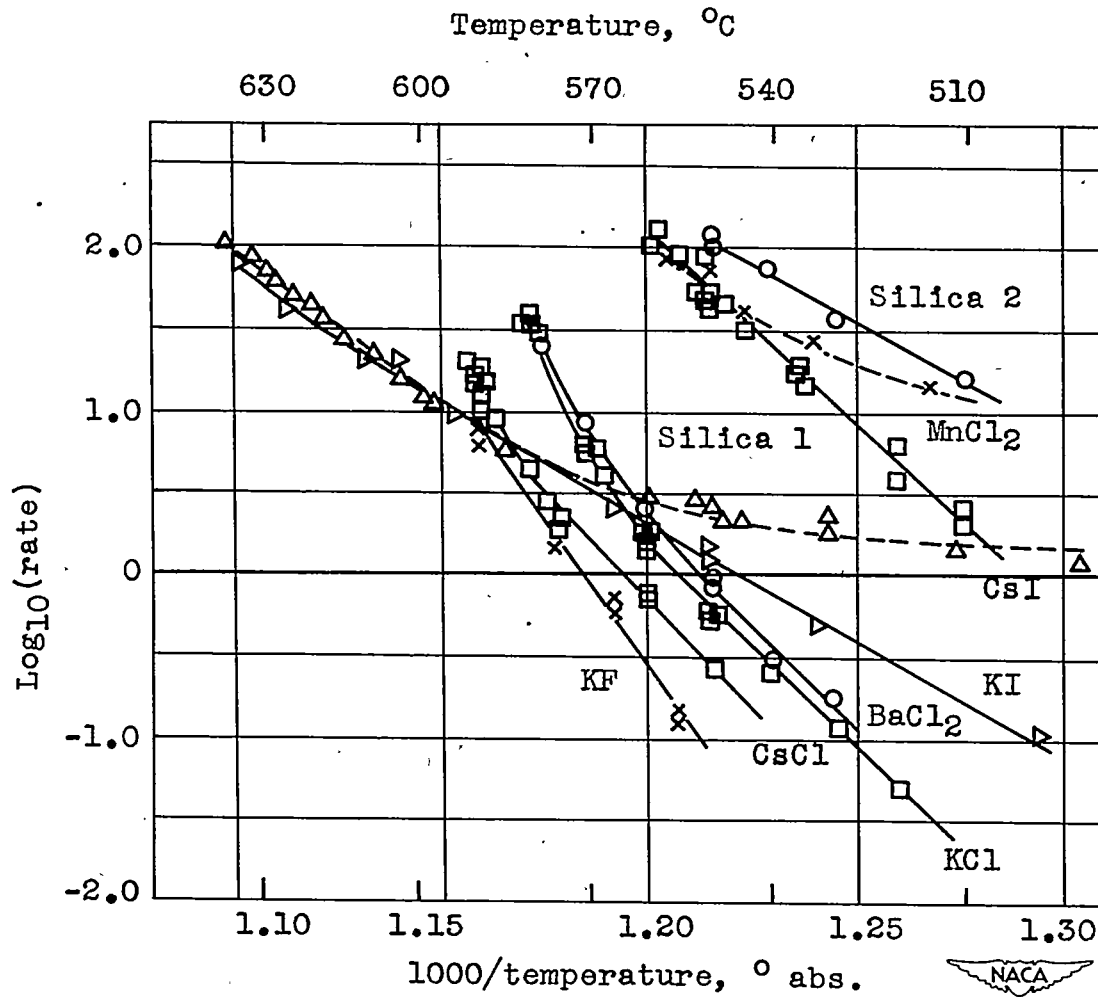


Figure 7. - Effect of different salts on rate of hydrogen-oxygen reaction at different temperatures (reference 48).