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**STUDY OF THE MECHANISMS OF FIRE EXTINGUISHMENT
OF PROPELLANTS**

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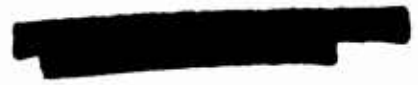
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AERONAUTICAL SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

FOREWORD

This report was prepared for the Flight Accessories Laboratory, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio, by the Division of Chemical Physics, Stanford Research Institute, Menlo Park, California, under Contract No. AF 33(616)-6583, Task No. 61331; "Study of the Mechanisms of Fire Extinguishment of Propellants." The technical administrator for Aeronautical Systems Division was Benito P. Botteri. At Stanford Research Institute the project supervisor was H. Wise and the project leader was W. A. Rosser, Jr. Work on the contract began on 1 November 1959. This report was completed April, 1961.

ABSTRACT

A study has been made of the inhibition of various premixed flames by two classes of chemicals: volatile halogen-containing compounds and finely divided powders. Some of each class were found to be very effective inhibitors of hydrocarbon combustion. Inhibition by volatile halogen compounds involves at least two types of reaction: (a) between chain carriers and the undecomposed halogen compound, and (b) between chain carriers and the decomposition or oxidation products of the halogen compound. Inhibition by powders probably involves these successive steps: (a) heating the powder particles to a high temperature by the hot flame gases, (b) partial evaporation of the powder particles, (c) decomposition or reaction of the evaporated material to provide metal atoms, and (d) inhibition of the combustion process by the liberated metal atoms -- these are believed to impede combustion by deactivating excited molecules which may be important intermediates in the burning process.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



WILLIAM C. SAVAGE
BRANCH CHIEF
Environmental Branch
Flight Accessories Laboratory

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I INTRODUCTION

The purpose of this study of fire extinguishment is to compare the ability of various substances to inhibit combustion and, where possible, to determine the mechanisms of such inhibition.

Some materials retard combustion by physically separating fuel and oxidizer or by cooling the flame gases. Other materials interfere chemically with the combustion process; in these cases, less material is required to suppress combustion than in physical interference. Because our knowledge of the pertinent chemistry is limited, usually it is not possible to predict which combustion systems are sensitive to chemical interference, or to identify the significant reactions, or to predict the usefulness of a given chemical. Therefore in this study it was necessary to proceed empirically by investigating various flame-inhibitor combinations.

II EXPERIMENTAL DETAILS AND RESULTS

The inhibitors which were used logically divide into compounds such as PCl_3 , which are volatile at room temperature, and powdered materials such as NaHCO_3 , which are not volatile at room temperature. In both cases the effectiveness of the additive was examined only in premixed flames.

A. Halogen-Containing Compounds in Methane- O_2 - N_2 Flames

1. Materials and Techniques

The chemical substances, listed in Table I, were used as obtained from commercial sources. Compressed laboratory air was dried (prior to use) by passage through a bed of granular CaCl_2 . All experiments involved the flow of one or more gases which were metered with Fischer & Porter tri-flat flowmeters. Inhibitors which are liquid under ambient conditions were introduced into the system by means of an electrical vaporizer. Liquid inhibitor was displaced at a few hundredths of a milliliter per minute from a syringe whose piston advanced at a rate controlled by a servomechanism. The displaced liquid passed to a small electrically heated vaporizer located in the vertical arm of a glass T-tube. The vapor produced was mixed with and swept away by the surrounding gas stream. The partial pressure of inhibitor in the resulting mixture was always less than its saturation vapor pressure at ambient temperature. The inhibitor-combustible gas mixture was then used for either flame speed or quenching measurements.

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Table I
GASES AND VOLATILE LIQUIDS USED

<u>Substance</u>	<u>Purity*</u>	<u>Supplier</u>
CH ₄	>99%	Matheson
C ₃ H ₈	>99%	Matheson
NH ₃	100%	Matheson
O ₂	Ind. grade	General Dynamics Corp.
N ₂	Commercial dry	General Dynamics Corp.
A	100%	Matheson
PCl ₃	--	J. T. Baker Chemical Co.
POCl ₃	--	Matheson
BBr ₃	--	American Potash
BCl ₃	--	Matheson
BF ₃	--	Matheson

* Claimed by Supplier

For flame speed measurements the mixed gases were burned at the exit of a long Pyrex tube, 1/2 inch i.d. The visible cone was photographed with a Polaroid camera, the total area of the visible flame determined from measurements on the photographs, and the flame speed S computed from the relation

$$S = \dot{V}/A \quad (1)$$

where \dot{V} = the volumetric flow rate of gas, and A = the area of the visible flame. The experimental arrangements for flame speed measurements are shown in Fig. 1, Apparatus A.

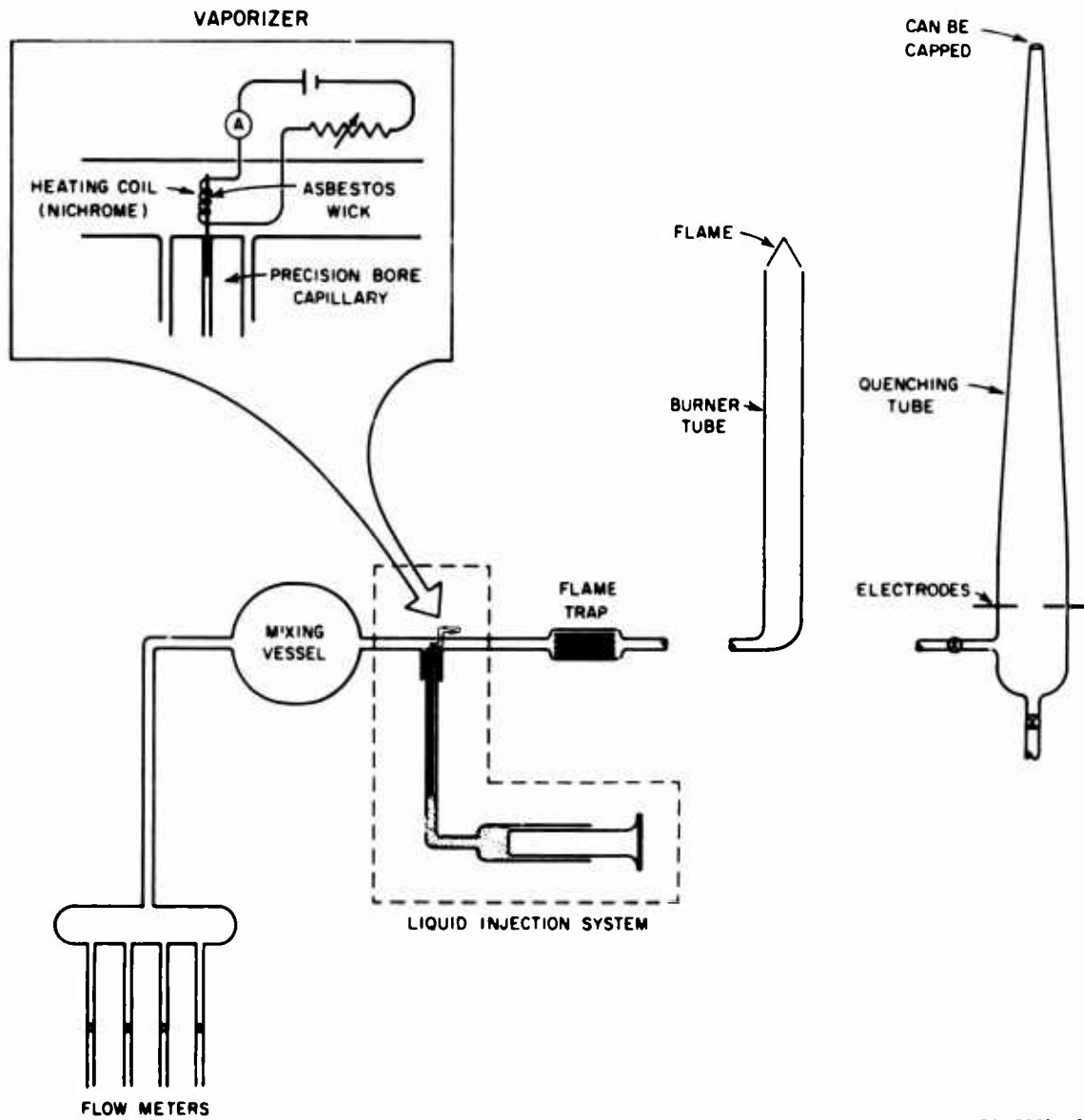
Quenching measurements were carried out using Apparatus B shown in Fig. 1. A special tube was employed consisting of a long tapered glass tube constructed to precise dimensions by the Fischer & Porter Co. Prior to actual quenching measurements a flow of premixed reactants through the system was established and held steady for about a minute. Past experience had revealed that some inhibitors are adsorbed on the walls of the quenching tube. Consequently, it was necessary to expose the quenching tube walls for a short time to the premixed reactants until no further adsorption of inhibitor occurred. Then the entrance flow line was closed, the narrow top of the quenching tube was capped by a rubber policeman, and the mixture within the tube was ignited by a high voltage spark. The portion of the flame which traveled down the tube was vented to and extinguished by the atmosphere, while the ascending flame rose until extinguished by the converging walls of the tube. The position of the flame at extinction was noted visually or was recorded by a photographic time exposure of the flame as it rose within the tube. The extinction point appeared on the positive film as the end of a light streak. The known inside diameter of the tube at the extinction point was considered to be the quenching distance.

2. The Quenching Effectiveness of HBr in Various CH₄-O₂-N₂ Mixtures

The effect of oxygen concentration on the ability of HBr to quench premixed CH₄-O₂-N₂ flames was studied. All mixtures contained stoichiometric proportions of CH₄ and O₂ while the ratio O₂/(O₂+N₂) was varied from 0.16 to 0.25. The experimental results, presented in Fig. 2, show that the quenching effectiveness of HBr decreases rapidly with increasing concentration of O₂. As the significant variable in these results is probably the flame temperature, it may be concluded that an increase in flame temperature adversely and seriously affects the quenching effectiveness of HBr and similar compounds.

3. Volatile Compounds in CH₄-air Flames

A number of compounds were tested for inhibition effectiveness by measuring their effect on flame speeds and on quenching distances of premixed CH₄-air flames. The compounds tested were: SF₆, BCl₃, BF₃, BBr₃, PCl₃, and POCl₃. The first three were much less effective than the last three.



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FIG. 1
 FLAME SPEED AND QUENCHING APPARATUS SCHEMATIC DIAGRAM

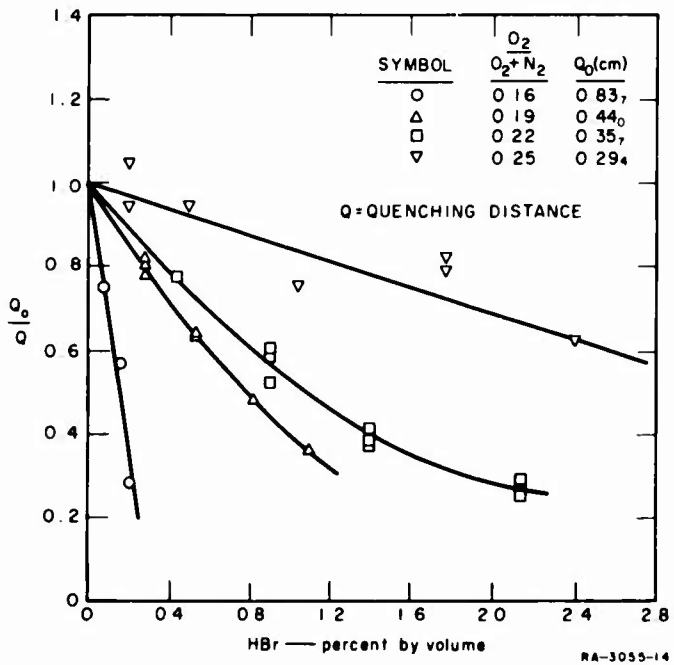


FIG. 2
 $CH_4-O_2-N_2-O_2$ CONCENTRATION VERSUS
 QUENCHING EFFECTIVENESS OF HBr

For near-stoichiometric CH₄-air flames the addition of a few tenths of a mole percent of SF₆, or BCl₃, or BF₃ to the combustible mixture increased quenching distance to some extent. The degree of effectiveness -- measured by the rate of increase of quenching distance Q with mole fraction x of inhibitor -- is listed in Table II, along with the value for HBr. In the case of BCl₃ and BF₃ the observed effectiveness indicated some chemical interference with the combustion process.

The compounds, BBr₃, PCl₃, and POCl₃, were found to be very effective inhibitors whether measured by changes in flame speed or in quenching distance. Quenching distance was observed to increase linearly with mole fraction of inhibitor. An example of this variation is shown in Fig. 3, where the slope is a measure of inhibitor effectiveness. Table II shows that BBr₃, PCl₃, and POCl₃ are comparable in effectiveness and are three to four times as effective as HBr.

Changes in flame speed were also used to measure inhibitor effectiveness for the cited compounds. With increasing inhibitor concentration, flame speed decreased but not linearly. Rather, the quantity 1/S² was found to increase linearly with inhibitor concentration. Examples are shown in Fig. 4, where the slope d(1/S²)/dx may be taken as a measure of inhibitor effectiveness. By this criterion PCl₃ and POCl₃ are comparable and each is about three times more effective than BBr₃ (see Table III). Previously acquired data for HBr when expressed in the same terms reveal that PCl₃ and POCl₃ are ten to fifteen times as effective as HBr.

The linear increase of 1/S² with x₁ is consistent with the identification of S² with an average reaction rate as represented by Eq. 2.

$$S^2 = k\bar{\omega}, \quad (2)$$

where k contains all the physical factors which affect flame speed and $\bar{\omega}$ is an average reaction rate in the flame (Ref. 1). In many cases of inhibited chain reactions the rate of reaction r has the form (Ref. 2)

$$r = \frac{a}{1 + bx} \quad (3)$$

where x is the concentration of inhibitor. By analogy $\bar{\omega}$ may be expressed in the same way and the dependence of flame speed on inhibitor concentration has the form

$$\frac{S_0^2}{S^2} = 1 + bx. \quad (4)$$

The constant "b" can be obtained from the slope

$$\frac{d(1/S^2)}{dx} = \frac{b}{S_0^2}. \quad (5)$$

In isothermal systems the term "b" is related to the rate constants associated with the chain-terminating reactions (Ref. 2). Again by analogy, "b" may have an equivalent significance for flame reactions.

Table II

EFFECT OF VARIOUS VOLATILE INHIBITORS ON
 QUENCHING DISTANCE OF PREMIXED CH₄-AIR FLAMES

Compound	dQ/dx_i (MM)	% CH ₄ by Volume in Mixture
SF ₆	0.4×10^2	9.5
BCl ₃	1×10^2	9.5
BF ₃	1×10^2	9.5
BBr ₃	6.2×10^2	9.1
PCl ₃	8.6×10^2	8.6
POCl ₃	7.6×10^2	9.1
HBr*	2×10^2	9.5

Q = quenching distance

x_i = mole fraction of inhibitor in the mixture

* The rate of increase of quenching distance with mole fraction of HBr, dQ/dx_i , increases with increasing concentration of HBr. The cited value¹ refers to the limiting value

$$\lim \frac{dQ}{dx_i} \Big|_{x_i \rightarrow 0}$$

Table III

EFFECT OF VARIOUS VOLATILE INHIBITORS ON
FLAME SPEED OF PREMIXED CH₄-AIR FLAMES

<u>Compound</u>	$\frac{d(\frac{1}{S^2})}{dx_i} \left(\frac{\text{sec}^2}{\text{cm}^2} \right)$	<u>% CH₄</u>
BBr ₃	0.77	8.6
BBr ₃	0.57	10.54
PCl ₃	1.8	8.6
PCl ₃	1.4	10.54
POCl ₃	1.8	8.6
POCl ₃	1.5	9.1
POCl ₃	1.7	10.54
HBr*	0.11	9.6

S = flame speed

x_i = mole fraction of inhibitor

* For HBr, the quantity $\frac{d(\frac{1}{S^2})}{dx_i}$ increases with increasing concentration of HBr. The cited value $\frac{d(\frac{1}{S^2})}{dx_i}$ refers to the limiting value,

$$\lim_{x_i \rightarrow 0} \frac{d(\frac{1}{S^2})}{dx_i}$$

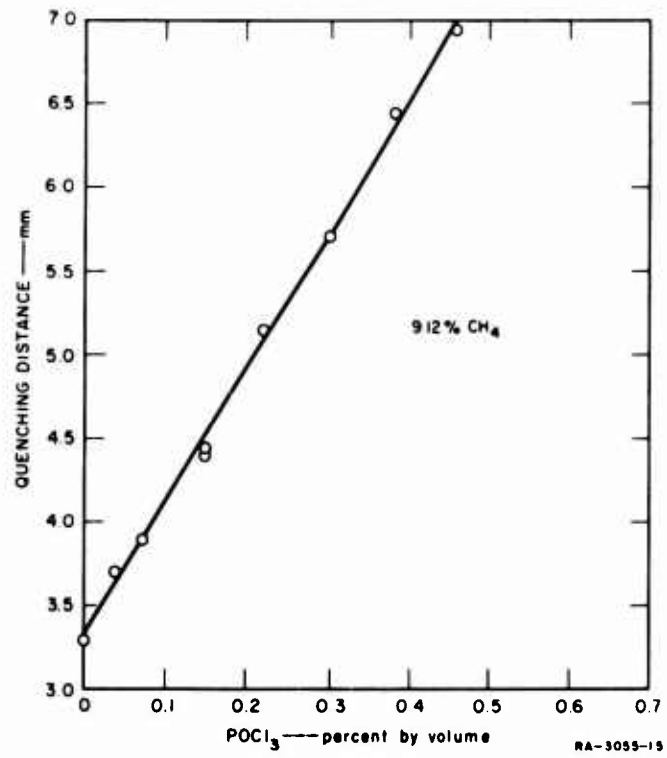


FIG. 3
 CH₄-AIR—QUENCHING DISTANCE VERSUS
 CONCENTRATION OF POCl₃

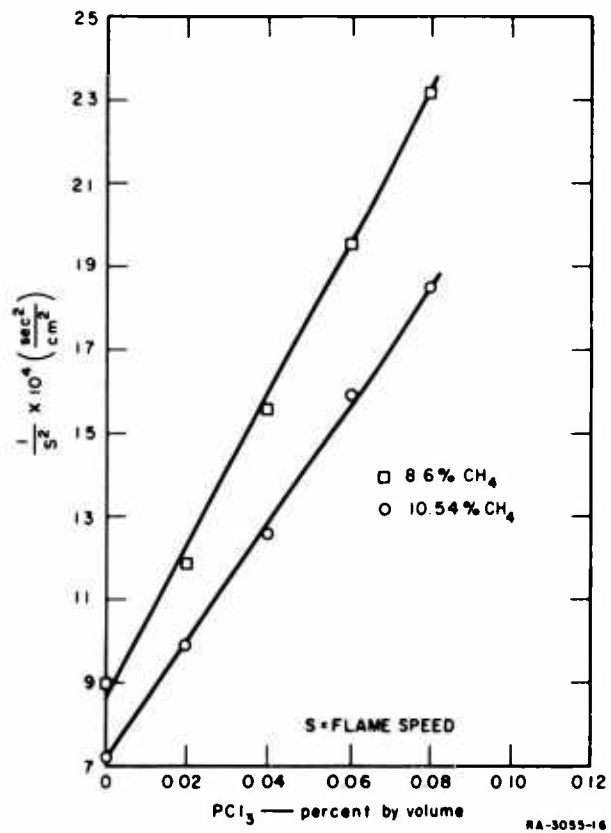


FIG. 4
 CH_4 -AIR — $1/S^2$ VERSUS CONCENTRATION
 OF PCl_3

Comparison of quenching data with flame speed data indicates that BBr_3 , and particularly PCl_3 , and POCl_3 affect flame speed more than quenching distance. This is also revealed by the fact that the product SQ for a given CH_4 -air composition decreased markedly with increasing concentration of inhibitor. Existing theories of flame quenching (Refs. 3 and 4) based on heat loss in laminar flame propagation imply that the product $\text{Q}\cdot\text{S}$ should remain constant. It is apparent that these theories are not sufficiently detailed to permit full analysis of chemical inhibition.

B. Finely Dispersed Powders in Premixed Flames

1. Materials and Techniques

The gas handling procedure and equipment were similar to those described in Section IIA1. Two additional gases, NH_3 and C_3H_8 , were used; both were C.P. materials obtained from the Matheson Co.

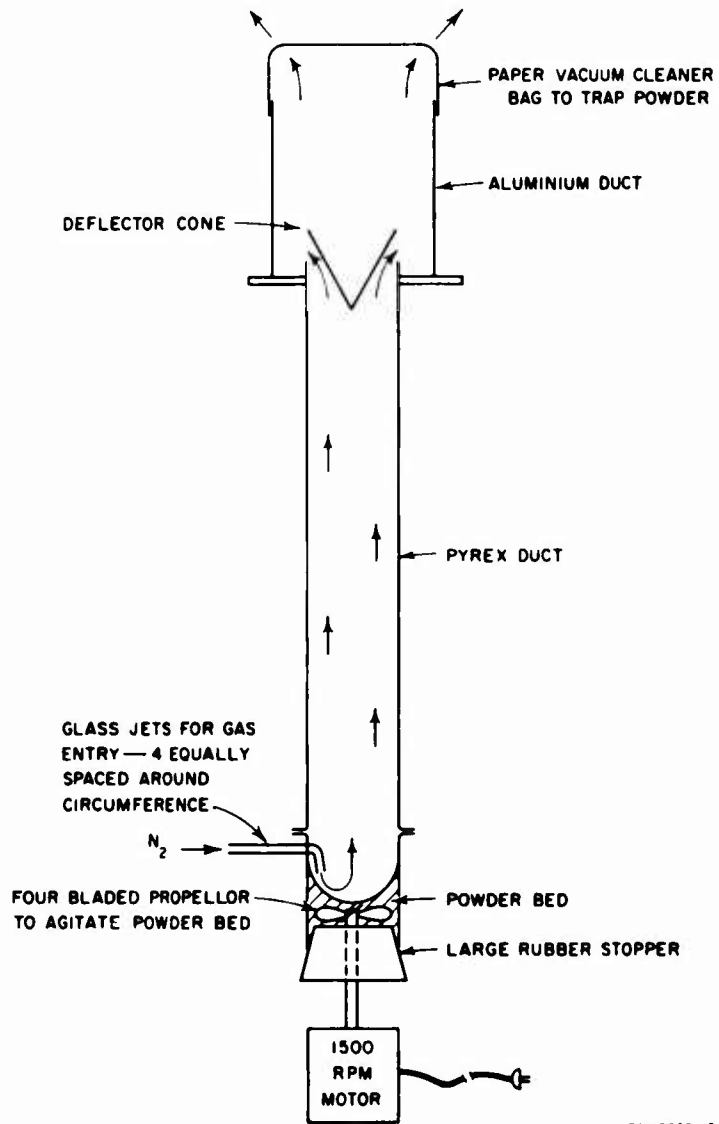
All the powders were C.P. anhydrous materials available either as powders or as finely crystalline materials. Some were of sufficient fineness to be used without further treatment; most, however, required some size reduction. These were wet milled with acetone in a small laboratory ball mill; to avoid contamination, the mill was an unlined ceramic jar and the grinding elements were small ceramic-coated metal cylinders. After milling, the powder was first air dried under a heat lamp to remove the bulk of the acetone and then oven dried at about 110°C . The dry powder cake was pulverized by brief ball milling and sieved through a 250 or a 325 mesh stainless steel screen.

Milled powders contained a wide range of particle sizes. Two methods of size separation were tried, sieving and gas elutriation. Sieving by means of micromesh screens* was attempted, but inasmuch as the screens plugged quickly the method was abandoned. Gas elutriation with dry N_2 was tried using the device shown in Fig. 5; this was inefficient and slow except at high gas flow rates; some size reduction could be obtained but not as much as desired. Consequently, gas elutriation was used only for special purposes and not as a standard procedure.

2. The Dispersal of Powder in a Combustible Gas

Several simple powder generators were tried and found wanting. Most of the powders used were neither free-flowing nor easily dispersible. Furthermore, in order to interpret the experimental results it was considered advisable to use only pure materials and, if possible, to avoid the use of additives which would complicate analysis. Eventually a dispersing device was devised which performed satisfactorily for most cases. The powder generator, (Fig. 6), consisted of a Pyrex cylinder (6 cm i.d.) fitted at each end with large rubber stoppers. The generator was provided

* Buckbee Mears Co., St. Paul, Minn.



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FIG. 5
 SCHEMATIC DIAGRAM OF
 GAS ELUTRIATION DEVICE

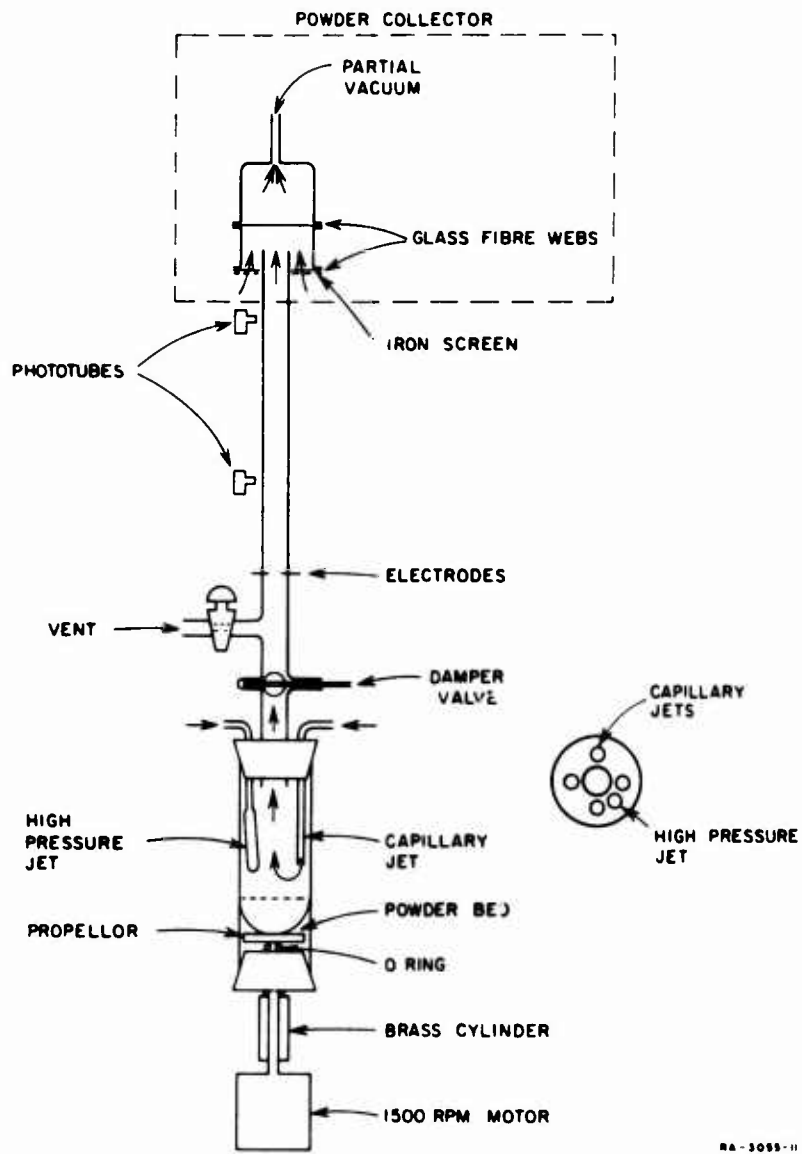


FIG. 6
POWDER GENERATOR AND FLAME TUBE SCHEMATIC DIAGRAM

with five jets through which gas could enter the system, a four-bladed propeller to agitate the powder bed, and an exit tube for the gas-powder mixture. The propeller was driven by a 1500 RPM electric motor. Four of the gas jets were made from glass tubing by melting the end of the tube until the open end had shrunk to about 1 mm in diameter. The fifth jet, used only to obtain high powder concentrations, was made from brass tubing with a hemispherical cap through which five holes 0.015 inch in diameter had been drilled. One of these holes was on the axis of the tube, the other four were arranged symmetrically around it. The gas emerging from these holes was very effective in picking up powder from the powder bed.

To obtain a powder-gas mixture the output of the mixing system was split by means of needle valves into two streams; one passed directly to the vertical output tube of the powder generator, and the other entered the powder generator through the glass jets and reunited with the first. The concentration of powder in the final mixture could be changed by varying the relative amounts of the two gas streams up to the point when all of the gaseous mixture passed through the generator. If even higher powder concentrations were desired, it was again necessary to split the gas flow, this time into a fraction which entered the generator through the four glass jets and the remainder through the metal jet. In this manner it was possible to obtain powder concentrations up to about 10% by weight of the gas flow. Substantial flow through the metal jet required an upstream pressure as much as 300 mm Hg greater than ambient.

3. Measurement of the Effect of Powder on Combustion

The gas-powder stream emerging from the powder generator was used in three different types of measurement. Two of these provided data of limited value; the third was more successful.

For an appropriate flow rate the exit tube from the generator can be used as a Bunsen burner. It was found, however, that such a flame was sensitive to the presence of powder such as NaHCO_3 in the gas stream and tended to blow off the burner and could not be reignited without stopping the flow of powder. Prior to the point of blow-off an increase in flame size, i.e., reduction in flame speed, was noted but could not be accurately measured. The presence of gaseous sodium and of hot particles in the flame resulted in a diffuse appearance which did not lend itself to photographic measurement of flame size. Only with an inert powder such as talc was it possible to measure the effect of powder concentration on flame speed. Consequently, the Bunsen burner method was abandoned.

In the second approach a tapered quenching tube was used as an exit tube for the gas-powder mixture in the generator. For this purpose a cylindrical extension of the large end of the quenching tube was inserted into the generator. The gas-powder mixture then flowed upward through the tube. Quenching measurements were made in a manner similar to that described

in Section IIA1. It was found that quenching distance increased significantly as the concentration of NaHCO_3 in the mixture was increased. However, the quenching data obtained were erratic and of limited usefulness. Consequently, this method too was abandoned.

The third approach was the most successful, and the bulk of our measurements were obtained by this method. A long glass cylinder about 2 cm in diameter was inserted a short distance into the generator as shown in Fig. 6. The exit gases from the generator flowed vertically upward through the tube and were vented to the atmosphere at the top. After a steady flow of gas-powder mixture had been established, the powder output was measured by collecting on a glass filter paper* the powder content of the gases. A collection time of 30 or 60 seconds was usually sufficient to give a weighable amount of powder on the filter. The weight concentration of powder in the gas was calculated from the weight of collected powder and the flow rate of the gas stream. Immediately after a powder sample had been collected, the gas supply to the generator was stopped, the damper valve closed, the side vent opened to the atmosphere, the open end of the tube capped with a rubber stopper, and the mixture ignited by means of a spark. The time required for the flame to travel between two fixed points on the tube was measured by phototubes. The phototube signals were displayed on an oscilloscope face and photographed by Polaroid camera. The average propagation velocity of the flame was calculated from the known distance between the phototubes and the measured time of transit.

In the absence of powder the flames were approximately hemispherical in shape; after the first few inches of travel, they moved through the tube at an apparently uniform rate. Slight tilting of the flame was sometimes observed. The presence of powder at times resulted in irregular flame shapes. Because the propagation velocity v is related to flame speed by

$$v = S \frac{A_f}{A_t} \quad (6)$$

where A_f = the area of the flame and A_t = cross sectional area of the tube, these perturbations of flame shape are a source of error. The measured value of v will be large compared with values of v corresponding to unperturbed flame shape. In extreme cases, tube flames were extremely long and highly tilted. The very large ratio of A_f/A_t for such flames gave very high values of v even though S itself was small. These tilted flames were frequently encountered and they are believed to occur because of a non-uniform distribution of powder in the tube. Even in the absence of unsymmetrical perturbations in flame shape, the ratio A_f/A_t increased from about 2 for an uninhibited methane-air flame to about 4 for the slowest flames measured. This variation, however, was systematic.

* Mine Safety Appliances Co.

4. Measurement of Particle Size and of Specific Surface Area

Specific surface area of experimental powders was measured by an optical method using an apparatus modeled after one described in Ref. 5. When the optical cell contains a uniform dispersion of powder in a suitable liquid medium, the optical density of the dispersion is related to the concentration of powder by Eq. 7 (Ref. 6).

$$- \ln \xi = kcl \int_0^{\infty} K_r n_r \pi r^2 dr \quad (7)$$

where

- ξ = optical transmission
- c = powder concentration in gms/cc
- l = optical path length (5 cm in this case)
- k = a dimensionless shape factor (~ 1)
- K_r = ratio of optical cross section to geometric cross section for particles of radius r
- n_r = number of particles of radius r in one gram of powder.

If the powder particles are permitted to settle from the suspension, Eq. 7 refers to the initial dispersion. At later times Eq. 7 must be replaced by Eq. 8

$$- \ln \xi = kcl \int_0^{R(t)} K_r n_r \pi r^2 dr \quad (8)$$

$R(t)$, the radius of the largest particle present in the light beam at time t , may be calculated by assuming that the individual particles settle at a rate which can be calculated from Stoke's law. Consequently, from measurement of $-\ln \xi$ as a function of time it is possible to derive the size distribution of particles (Ref. 6). For our purposes the method was simplified by assuming $k = 1$, and $K_r = 2$ for all values of r of interest (see Refs. 5 and 6). Then the total specific area of the powder, A^* , can be calculated from Eq. 9.

$$A^* = - \frac{4 \ln \xi_i}{2 cl} \quad (9)$$

The specific surface area data listed in Table IV were calculated using Eq. 9. The cited simplifications were also used during particle size analysis determined from the chart record of optical density versus time.

In the experimental measurements about 20 mg of powder was thoroughly dispersed in about 300 ml of acetone contained in the optical cell and the measurement of optical density was begun. The initial portion of the chart record was disturbed by movement of the cell fluid resulting from the earlier mixing process. This movement disappeared in a short time, and the initial optical density was determined by extrapolation of the chart record back to time zero. When size analysis was desired, the optical density was recorded for the half hour or so required for reasonably complete settling of the powder sample.

Table IV
 SPECIFIC AREA OF POWDERS USED

<u>Powder</u>	<u>A*(cm²/gm)</u>	<u>\bar{d}(μ)</u>
talc	12,600	2.4
Ca(OH) ₂	9,000	2.9
CaCO ₃	2,000	11
NaBr	2,000	9
CaF ₂	3,500	5.4
NaF	3,300	6.5
CuCl	3,000	5.7
NaCl	4,500	6.0
K ₂ SO ₄	5,200	4.3
NaHCO ₃	7,760	3.5
NaHCO ₃	11,900	2.3
KHCO ₃	12,400	2.2
Na ₂ CO ₃	4,940	4.9
Na ₂ CO ₃	10,800	2.2

$$\bar{d} = \frac{6}{\rho A^*}$$

\bar{d} = average particle diameter

ρ = density of material

A* = specific surface area

The surface data listed in Table IV were obtained in the manner described. The average particle size is defined by Eq. 10

$$\bar{d} = \frac{6}{\rho A^*} \quad (10)$$

where ρ is the density of the powder material. One gram of powder containing only particles of diameter \bar{d} would have the same surface area as one gram of the actual powder. Sedimentation analysis revealed that \bar{d} is only a crude measure of powder fineness. All powders listed in Table IV, even the coarse ones, contained a substantial number of particles of only 2 or 3 microns in diameter. For example, the weight distribution of NaF particles passed through a maximum at about $3\frac{1}{2}\mu$ although $\bar{d} = 6\frac{1}{2}\mu$.

The data in Table IV refer to samples collected at the exit of the flame tube in the manner discussed in Section IIB2. Comparison of that data with surface data for the powder initially present in the generator revealed little or no difference for fine powders ($A^* \approx 10,000 \text{ cm}^2/\text{gm}$). For coarse powders there was some difference. Exit material was finer than the original powder charge, indicating that the generator also functioned to some extent as an elutriation device. To avoid error from such elutriation only a few per cent of the initial powder charge in the generator was used in a related series of measurements. If necessary, the residue was discarded and replaced by a new charge.

5. The Effect of Powders on Premixed Flames

Several of the powders tested were not effective inhibitors of premixed CH_4 -air combustion. About 5 wt % of CaF_2 , talc, CaCO_3 , or $\text{Ca}(\text{OH})_2$ was required to reduce by 10% the speed at which a stoichiometric CH_4 -air flame propagated through a tube. This degree of speed reduction may be accounted for by physical interaction of the powder with the flame. Heat and momentum loss of the flame are sufficient to account for the observed results. On the other hand, the remainder of the powders tested, NaF, NaCl, NaBr, CuCl, K_2SO_4 , NaHCO_3 , KHCO_3 , and Na_2CO_3 , were effective inhibitors of CH_4 -air combustion to a degree which indicates chemical interference with the combustion process.

As shown in Fig. 7, relatively little Na_2CO_3 powder is required to produce a significant reduction in the propagation velocity of a stoichiometric CH_4 -air flame. These features should be noted: (a) the weight concentration of powder when expressed in mg/cc is very nearly the same as the weight fraction; (b) the observed scatter in the data is primarily due to perturbation of flame shape (see Section IIB2); (c) the ratio of flame area to tube area (apart from erratic perturbations) increases from about 2 at zero inhibitor concentration to about 4 at concentrations corresponding to points on the nearly horizontal portion of the curve; (d) the powder concentration corresponding to the intersection of the dotted straight lines may be used as a measure of inhibitor effectiveness. The lower this critical concentration, the more effective the inhibitor. For fine Na_2CO_3

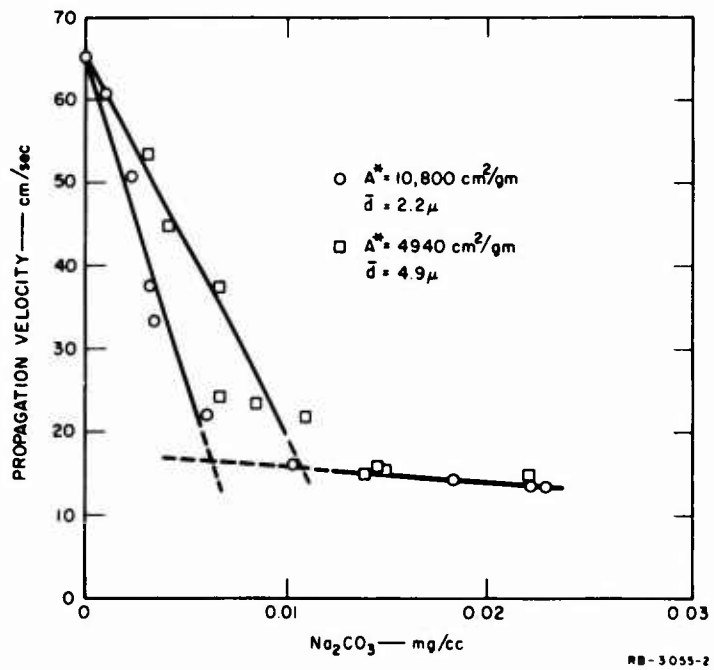


FIG. 7
 STOICHIOMETRIC CH_4 -AIR—THE EFFECT OF Na_2CO_2
 ON THE PROPAGATION VELOCITY

this intercept concentration is about 0.6 wt %, whereas for the coarser Na_2CO_3 the intercept concentration is about 1.1 wt %. Comparison of these values with the specific surface areas of the two powders indicates that powder effectiveness is approximately proportional to specific surface area.

As shown in Fig. 8, similar results were obtained using NaHCO_3 . Because of flame perturbations for low concentrations of NaHCO_3 , the relation between powder effectiveness and A^* could not be determined with precision. However, a size effect is clearly evident. In view of the fact that NaHCO_3 decomposes to Na_2CO_3 at relatively low temperatures, it is probable that the observed effectiveness of NaHCO_3 merely reflects the effectiveness of Na_2CO_3 . The data shown in Figs. 7 and 8 are consistent with this interpretation. The effect of KHCO_3 , $A^* = 12,400 \text{ cm}^2/\text{gm}$, on propagation velocity was measured (Fig. 9). Comparison with the data for NaHCO_3 , $A^* = 11,900 \text{ cm}^2/\text{gm}$, reveals that KHCO_3 powder is twice as effective as NaHCO_3 powder. It is noteworthy that KHCO_3 has been found to be twice as effective as NaHCO_3 as a fire extinguisher (Ref. 7). Because both NaHCO_3 and KHCO_3 decompose readily to the respective carbonates, the effective inhibitor in both cases is probably the alkali carbonate.

The effect of NaBr , NaCl , NaF , CuCl , and K_2SO_4 on stoichiometric CH_4 -air flames was also measured. Precise results were obtained for NaCl and CuCl (Figs. 10 and 11). Qualitatively NaBr , NaF , and K_2SO_4 were also effective inhibitors, but because of extreme flame instability precise data could not be obtained. This instability is apparently associated with poor dispersibility of the powder. For example, several experiments with NaCl , a poorly dispersible powder, gave unstable, tilted flames but after unusually prolonged milling and prolonged oven-drying of the NaCl powder it was possible to obtain the results shown in Fig. 10. Presumably a similar procedure would have been successful with NaBr , NaF , and K_2SO_4 . In contrast, a well-behaved powder such as CuCl involved no difficulties (see Fig. 11) and flame instability was not observed.

The effect of mixture ratio on powder effectiveness was investigated using CH_4 -air mixtures with CH_4 content varying from 8 to 12 per cent by volume. The test powder was NaHCO_3 , $A^* = 11,900 \text{ cm}^2/\text{gm}$. Results were similar to those shown in Fig. 8. Powder effectiveness for nonstoichiometric CH_4 -air mixtures was comparable with or slightly greater than for the stoichiometric flame. Differences were no greater than could be accounted for by virtue of the differences in propagation speed for the various mixtures.

Flame inhibition by dispersed powder is affected by oxidizer concentration. A stoichiometric CH_4 - O_2 flame diluted with N_2 so that $\text{O}_2/(\text{O}_2 + \text{N}_2) = 0.25$ required 1.7 wt % of fine Na_2CO_3 to reduce the linear speed from 142 cm/sec to the intercept point which in this case occurs at about 20 cm/sec (see Fig. 12). The increase in powder requirement reflects primarily

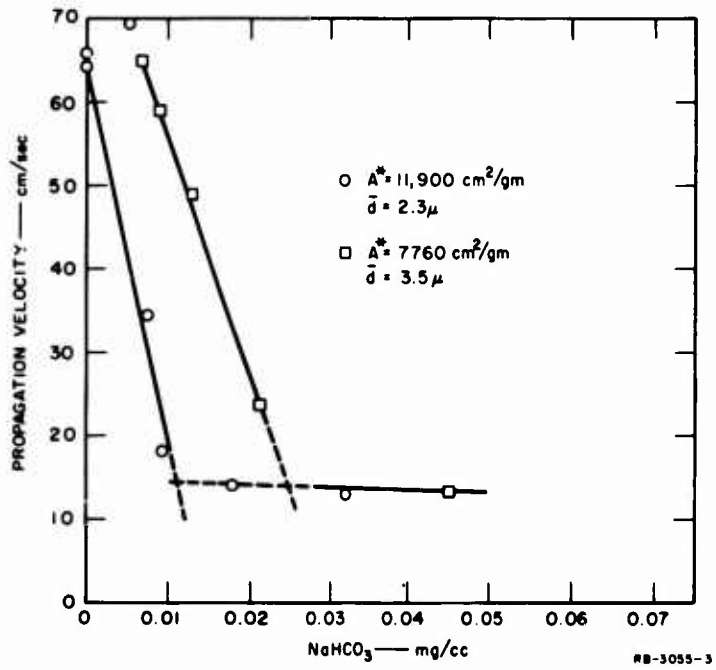


FIG. 8
 STOICHIOMETRIC CH₄-AIR — EFFECT OF NaHCO₃
 ON PROPAGATION VELOCITY

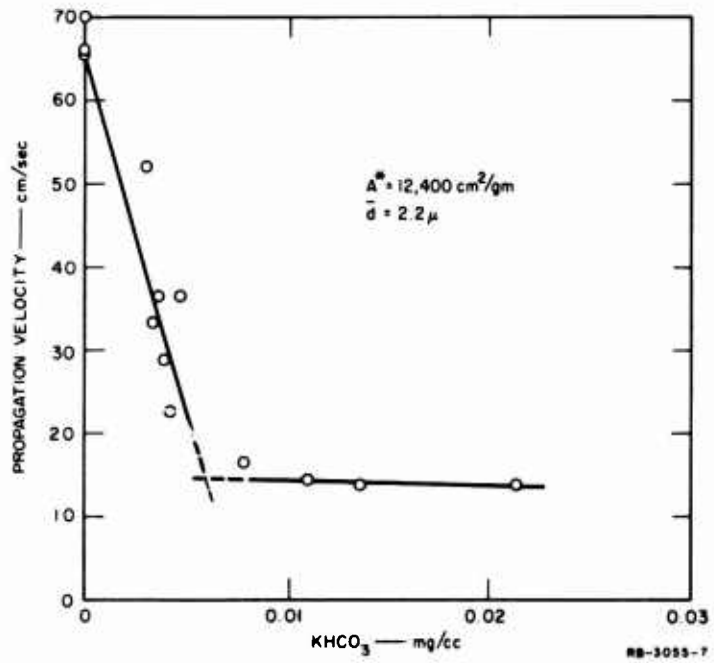


FIG. 9
 STOICHIOMETRIC CH₄-AIR—EFFECT OF KHCO₃
 ON PROPAGATION VELOCITY

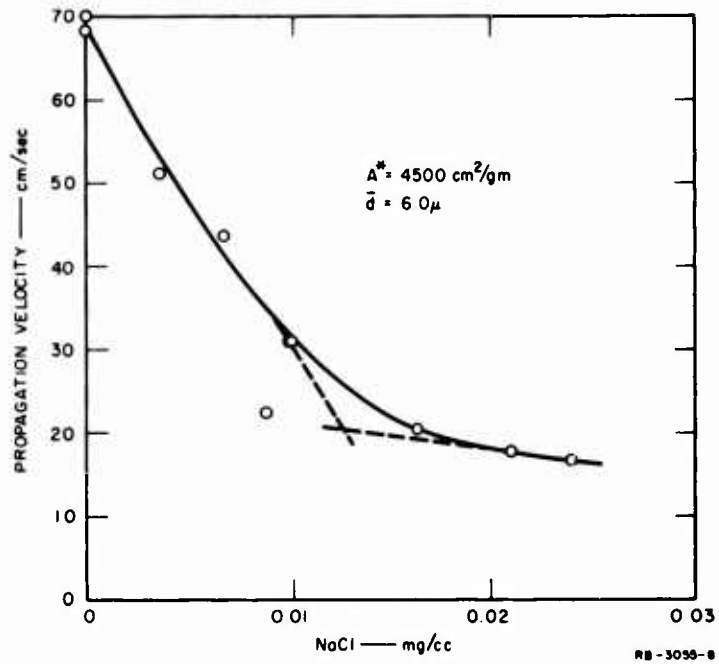
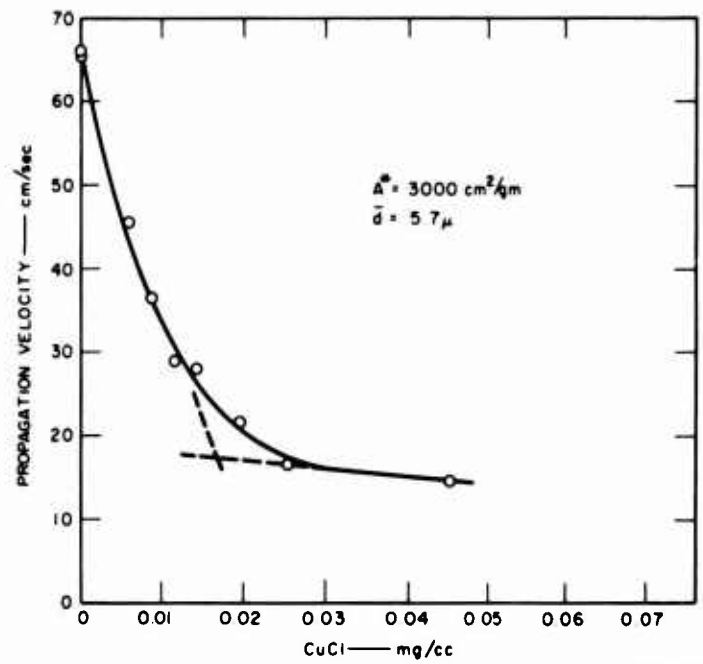


FIG. 10
 STOICHIOMETRIC CH_4 -AIR—EFFECT OF NaCl
 ON PROPAGATION VELOCITY



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FIG. 11
 STOICHIOMETRIC CH₄-AIR—EFFECT OF CuCl
 ON PROPAGATION VELOCITY

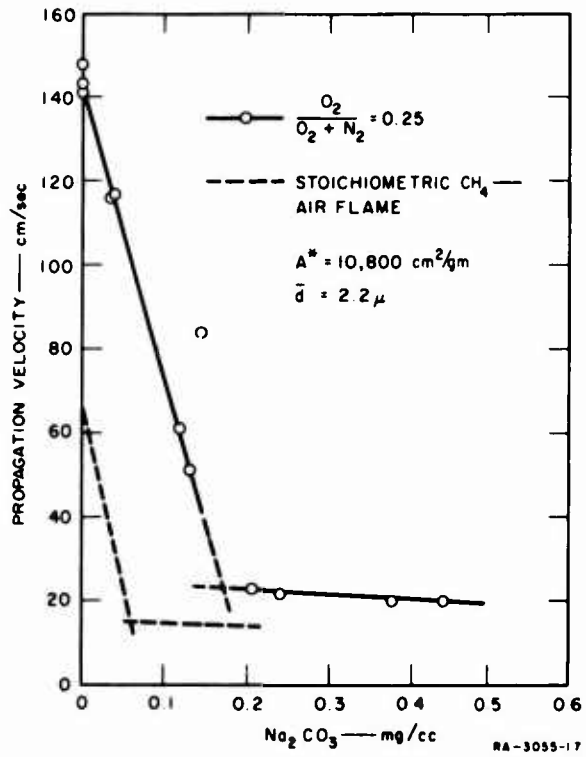


FIG. 12
 STOICHIOMETRIC CH_4 - O_2 - N_2 — THE EFFECT OF O_2
 CONCENTRATION ON THE EFFECTIVENESS OF Na_2CO_3

the higher initial propagation velocity. Support for this view is provided by another experiment using a $\text{CH}_4\text{-O}_2\text{-Argon}$ mixture with an initial propagation velocity very nearly the same as that for a stoichiometric $\text{CH}_4\text{-air}$ flame, 65 cm/sec. The effectiveness of KHCO_3 in the two cases was much the same, about 0.6 wt % powder. In contrast, the presence of about one per cent by volume of CH_3Cl in a stoichiometric $\text{CH}_4\text{-air}$ mixture considerably reduced the effectiveness of Na_2CO_3 although the CH_3Cl itself has very little effect on the initial propagation velocity of the mixture (see Fig. 13).

The effectiveness of Na_2CO_3 (or NaHCO_3) was found to vary with the nature of the fuel. About 2.5 wt % of Na_2CO_3 , $A^* = 10,800 \text{ cm}^2/\text{gm}$, was required to reduce the propagation velocity of stoichiometric $\text{C}_3\text{H}_8\text{-air}$ flame from 80 cm/sec to 20 cm/sec, compared with about 1 wt % for a stoichiometric $\text{CH}_4\text{-O}_2\text{-N}_2$ mixture of the same initial propagation velocity. The noncarbonaceous system $\text{NH}_3\text{-O}_2\text{-N}_2$ was found to be only slightly affected by powdered NaHCO_3 . An experiment using a near stoichiometric composition with an oxidizer concentration $\text{O}_2/(\text{O}_2 + \text{N}_2) = 0.4$ showed that 2 wt % of NaHCO_3 , $A^* = 11,900 \text{ cm}^2/\text{gm}$, only reduced propagation velocity from 62 cm/sec to 52 cm/sec.

III THE TEMPERATURE HISTORY OF SMALL PARTICLES EXPOSED TO A PREMIXED FLAME

During passage through a flame the individual particles of a dispersed powder will be heated and may partially evaporate. The heat transferred from the flame gases to the particles may not represent a significant thermal drain on the flame, but the evaporated material may affect the combustion reactions. Two problems must be considered: the degree of heating of small particles by the flame, and the extent of evaporation resulting from this heating. The two problems are coupled and in their entirety are extremely difficult to solve. After some simplification it was possible to obtain solutions which were adequate for our purposes.

The actual temperature profile through a premixed flame was replaced by the profile shown in Fig. 14, which has been divided into three zones: a preheat zone in which the temperature of the unburned gas rises exponentially with distance, a reaction zone in which the temperature rises linearly with distance, and a post-combustion zone of uniform temperature. The assumed temperature profile has been terminated at a definite position $x = \delta$, because where strong chemical inhibition occurs it must occur where the reaction rate is high, that is, in or near the visible flame. The reactions which take place in the post flame gases do so gradually over a distance large compared with the thickness of the visible flame. Particles in the region $x > \delta$ may affect these processes and will eventually reach thermodynamic equilibrium with the hot combustion gases. In this analysis, however, the region $x > \delta$ will not be considered. In addition, because the observed sensitivity of flame speed to the presence of some powders is far greater than can be accounted for by heat loss alone, the effect of the powder on T_a , the adiabatic flame temperature, has been neglected.

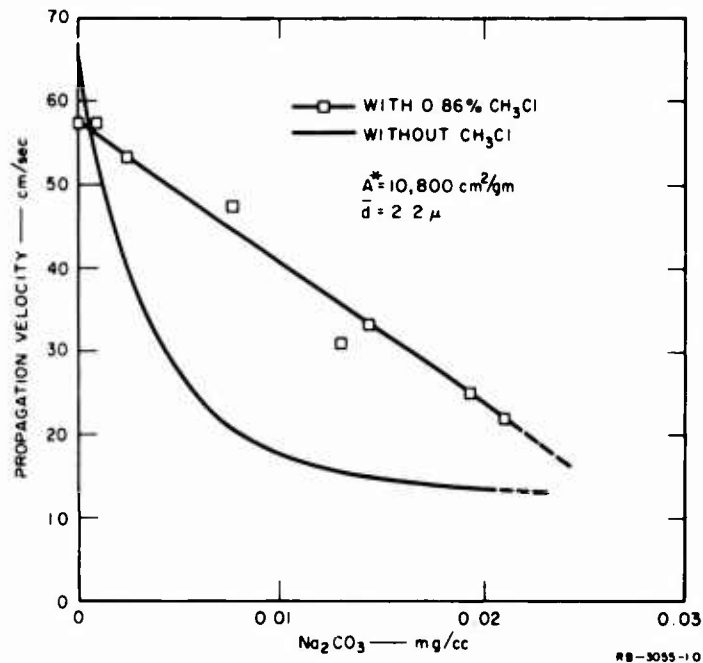


FIG. 13
 STOICHIOMETRIC CH₄-AIR — THE EFFECT OF CH₃Cl
 ON THE EFFECTIVENESS OF Na₂CO₃

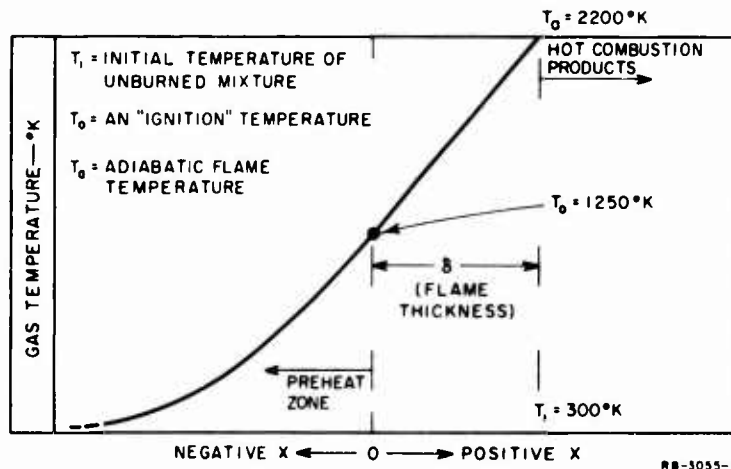


FIG. 14
 ASSUMED TEMPERATURE PROFILE FOR A
 STOICHIOMETRIC CH_4 -AIR FLAME

In the preheat zone the reaction rate is taken to be zero. Consequently the temperature profile has the form (Ref. 8)

$$\frac{T_1 - T_i}{T_0 - T_i} = \exp\left(\frac{c\rho_1 Sx}{\lambda}\right) \quad (11)$$

where

- ρ_1 = the initial gas density
- T_1 = the gas temperature at a point x
- T_i = the initial gas temperature
- T_0 = an ignition temperature
- c = the average heat capacity of the gas
- λ = the average thermal conductivity of the gas
- S = the flame speed
- x = distance from a fixed point in the flame.

The preheat zone ends at the point $x = 0$, where $T_1 = T_0$. For mathematical convenience T_0 is taken as the average of T_i and the adiabatic flame temperature T_a . The quantities c and λ should be values averaged over the temperature interval $T_0 - T_i$. Because c and λ also appear in calculations for the reaction zone, it is more convenient to evaluate c and λ at T_0 and use those values for both the preheat and the reaction zones.

The gas temperature in the reaction zone increases linearly from T_0 to T_a and can be represented by the expression

$$\frac{T_1 - T_0}{T_0 - T_i} = \frac{x}{\delta} \quad (12)$$

where $\delta = \frac{\lambda}{c\rho_1 S}$. Equation 12 is the tangent to Eq. 11 at the point $x = 0$. As shown in Fig. 14, the parameter δ is the thickness of the reaction zone, about 0.2 mm for a stoichiometric CH_4 -air flame.

In both the preheat and the reaction zones the time rate of temperature increase of a nonevaporating spherical particle has been represented by Eq. 13.

$$\rho_s c_s V_s \frac{dT}{dt} = 2\pi d \lambda (T_1 - T) \quad (13)$$

where

- V_s = volume of the particle
- d = diameter of the particle
- T_1 = the gas temperature
- T = the particle temperature
- c_s = specific heat of the particle material
- ρ_s = density of the particle.

The most important assumptions implied by Eq. 13 are:

- (1) The thermal conductivity of the particle material is very high, consequently the temperature within the particle is uniform and equal to the surface temperature
- (2) The course of particle heating may be regarded as a succession of incremental steady states
- (3) The Nusselt number for heat transfer equals 2.

These plausible assumptions simplified the mathematical problem but may have introduced some error. The first of these assumptions is the least serious. A rigorous treatment of a related problem, the temperature history of a small particle suddenly immersed in a large quantity of a hot gas, indicated that no significant error resulted from the assumption of uniform particle temperature.

A certain length of time is required to attain a steady state for either heat transfer or diffusion. For heat transfer, a measure of this time is the quantity $l^2/2\alpha$, where l is some characteristic distance, and α is the thermal diffusivity of the gas. Similarly, for diffusion a measure of the time is the quantity $l^2/2D$ where D is the diffusion constant of the evaporating material through the surrounding medium. For this problem α and D are of comparable magnitude, a few cm^2/sec . The characteristic distance l may be taken as the radius of the particle. For particles with radii less than 5 microns the time required for attainment of a steady state (for either diffusion or heat transfer) is found to be less than 10^{-7} sec, compared with the transit time through the flame which is greater than 10^{-4} sec. It may be concluded that the steady state assumption involves little or no error.

The applicability of the steady state assumption for heat transfer is implied when using a value of two for the Nusselt number. In addition, the cited value $\text{Nu} = 2$ is only valid for purely conductive heat transfer. For the very small particles with which we are concerned this is probably the case.

The velocity of a particle being swept along by a moving gas will always differ from that of the gas itself. The importance of this lag can be estimated by comparing the relaxation time associated with velocity lag to the transit time of the particle through the flame. The relaxation time for velocity lag is given by the expression $\tau_v = \frac{2r^2\rho}{9\eta}$ where r = radius of the particle, ρ = density of the particle, η = viscosity of the surrounding gas. This time τ_v is the time required for a particle initially at rest in a quiescent gas to accelerate as a consequence of gravitational pull to $(1 - \frac{1}{e})$ of the terminal velocity. The lag time τ_v was evaluated for various values of r , for $\rho = 2$ gms/cc, and $\eta = 490$ μpoises .

This value of η corresponds to air at about 1000°C. For $r = 1\mu$, $\tau_v = 0.9 \times 10^{-5}$ sec, and for $r = 5\mu$, $\tau_v = 2.3 \times 10^{-4}$ sec. The transit τ_v times of interest are in the range 10^{-4} to 10^{-3} sec. It appears that velocity lag is not a serious perturbation for small particles ($r \sim 1$ or 2μ) but will occur to some extent for larger particles ($r \sim 5\mu$). The effect of velocity lag will be to lengthen the time of exposure of the particle to the flame. The rate of heat transfer will not be significantly affected because of the low Reynolds number associated with small particles and the relatively low gas velocities used.

Equation 13 may be converted to a form involving "x" rather than "t" by means of the relation

$$\frac{dT}{dt} = \bar{v} \frac{dT}{dx} \quad (14)$$

where \bar{v} is the average velocity of the gas-powder mixture. The use of a single average velocity for both gas and powder requires that the particles be small enough to follow the gas flow.

The integral of Eq. 13 for values of $x < 0$ is given by

$$\frac{T - T_i}{T_0 - T_i} = \frac{\phi \delta e^{x/\delta}}{1 + \phi \delta} \quad (15)$$

where

$$\phi = \frac{12 \lambda}{\bar{v} c_s \rho_s d^2} \quad (16)$$

Based on the conservation of mass equation the average flow velocity of the gas-powder mixture, \bar{v} , is approximately equal to 4S for near-stoichiometric CH₄-air flames. For values of $x > 0$, the integral of Eq. 13 is given by

$$T = T_0 + (T_0 - T_i) \left[\frac{e^{-\phi \delta (\frac{x}{\delta})} + \phi \delta (\frac{x}{\delta}) - 1}{\phi \delta} - \frac{e^{-\phi \delta (\frac{x}{\delta})}}{1 + \phi \delta} \right] \quad (17)$$

and at $x = \delta$,

$$T_w = T_0 + (T_0 - T_i) \left[\frac{e^{-\phi \delta} + \phi \delta - 1}{\phi \delta} - \frac{e^{-\phi \delta}}{1 + \phi \delta} \right] \quad (18)$$

The particle temperature within the reaction zone is seen to depend on the product parameter $\phi \delta$ and on the dimensionless distance-ratio x/δ . The particle temperature at the end of the reaction zone is a function of $\phi \delta$ alone.

The temperature T_w has been calculated as a function of particle size for these specific values: $c_s \rho_s = 2/3$ and 1, $\bar{v} = 4S$, $\lambda = 2 \times 10^{-4}$ cal $\text{cm}^{-1} \text{sec}^{-1} \text{deg}^{-1}$, $\rho_i = 1 \times 10^{-3}$ gms cm^{-3} , $c = 1/4$ cal $\text{gm}^{-1} \text{deg}^{-1}$, and $S = 40, 25, 15,$ and 10 cm sec^{-1} . The cited values for $c_s \rho_s$ are intended

to represent NaCl and NaF respectively. The variation of T_w with particle size is shown in Fig. 15. It is clear from the figure that the degree of particle heating can be great and that particle temperature can rise high enough to result in evaporation of materials not usually considered volatile.

In an isothermal system the steady state molar rate of flow, ψ_M , of material M diffusing away from a sphere of radius r may be represented by

$$\psi_M = -4\pi Drn \ln \left(1 - \frac{n_1}{n}\right) \quad (19)$$

where n = total molar concentration
 n_1 = molar concentration of "M" at the surface of the sphere
 D = diffusion constant of "M".

If the ratio $n_1/n \ll 1$, Eq. 19 may be approximated by

$$\psi_M = 4\pi Dr n_1 \quad (20)$$

Relative to unevaporated material, the enthalpy flow ψ_L associated with the molar flow, ψ_M , is given by

$$\psi_L = 4\pi Dr n_1 L \quad (21)$$

where L is the molar heat of evaporation. In a nonisothermal system such as a flame the material diffusing away from a particle will be further heated as it diffuses. This enthalpy increase, however, is small, compared with L which is about 40 to 50 kcal/mole for the materials we will consider, and therefore it will be neglected. The diffusion and heat transfer processes are then coupled only at the surface of the particle. As in the case of heat transfer alone, it is assumed that steady state expressions can be used to describe the rate at which mass and heat are transferred.

Evaporation (an endothermic process) is limited by, and can proceed only to, the extent that heat is provided to maintain the process. The rate of heat transfer, q, from the flame gases to a particle is given by

$$q = 2\pi d\lambda (T_1 - T) \quad (22)$$

Initially, $q \gg \psi_L$, and both the particle temperature and n_1 increase. Eventually there may arrive a time when $q = \psi_L$ and evaporation may be regarded as having begun at that time. Further addition of heat to a particle will result primarily in evaporation and only secondarily in an increase in particle temperature. This temperature increase is not thermally significant but is important in that n_1 is a strongly varying function of particle temperature. The temperature at which evaporation may be considered to have begun can be obtained by equating Eqs. 21 and 22.

$$\lambda (T_1 - T) = n_1 L D \quad (23)$$

The quantity n_1 is related to particle temperature by

$$n_1 = A e^{-L/RT} \quad (24)$$

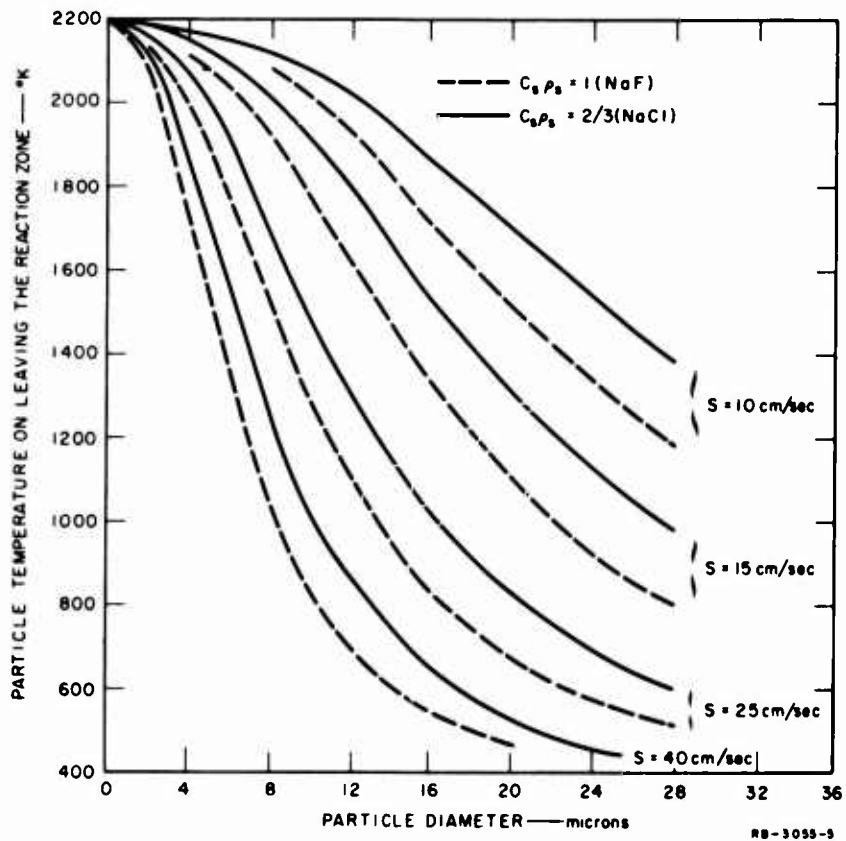


FIG. 15
 THE TEMPERATURE REACHED BY SMALL NONEVAPORATING PARTICLES
 DURING PASSAGE THROUGH A STOICHIOMETRIC CH_4 -AIR FLAME

Equation 24 when substituted in Eq. 23 results in

$$T_1 - T = \frac{A e^{-L/RT} D L}{\lambda} \quad (25)$$

The initial evaporation temperature is that temperature T_e consistent with Eqs. 12, 17, and 25 (for $x > 0$).

By graphical methods (see Fig. 16) T_e was determined as a function of particle size for NaCl and NaF. The necessary thermodynamic data were obtained from Ref. 9 and used to derive expressions of the type Eq. 24 for n_1 . For NaCl these data were used: B.P. = 1738°K, L at B.P. = 41 kcal/mole, $D = 4 \text{ cm}^2/\text{sec}$. The quantity n_1 was represented by

$$n_1 = 0.924 \times 10^{-8900/T} \text{ moles/cc} . \quad (26)$$

For NaF these data were used: B.P. = 1977°K, L = 48 kcal/mole, $D = 4 \text{ cm}^2/\text{sec}$, and n_1 was represented by

$$n_1 = 1.12 \times 10^{-10,400/T} \text{ moles/cc} . \quad (27)$$

In both cases the diffusion constant D is an estimated value.

The variation of T_e (initial) with particle size is shown in Fig. 16. Because S and r enter into the parameter ϕ in the same way, once T_e is known as a function of particle size for a given flame speed, T_e can readily be calculated as a function of size for other flame speeds. For either NaCl or NaF the initial evaporation temperature increases with increasing particle size up to a maximum value, $T_e(\text{max})$. The temperature of an evaporating particle cannot exceed (although it will reach) $T_e(\text{max})$ at $x = \delta$ unless the particle evaporates completely during passage through the flame. For NaCl, $T_e(\text{max}) = 1480^\circ\text{K}$, and for NaF, $T_e(\text{max}) = 1650^\circ\text{K}$.

Equation 20 implies that a particle evaporating under steady state conditions will decrease in size at a rate described by the expression

$$d^2 = d_0^2 - \frac{8 M D n_1 t}{\rho_s} \quad (28)$$

where $M =$ molecular wt of the material.

A similar steady state expression can be derived for a particle evaporating in a flame

$$d^2 = d_0^2 - \frac{8 M \lambda}{\rho_s L} \int_0^t (T_1 - T) dt . \quad (29)$$

In Eq. 29, n_1 has been eliminated by means of Eq. 23. Time is measured from the onset of evaporation as previously defined. Let x_e be the point in the flame corresponding to this time. In the cases we will consider, $x_e > 0$. This distance will be traversed in a time $\tau = (\delta - x_e)/\bar{v}$. Equation 29 may therefore be expressed

$$\frac{d^2}{d_0^2} = 1 - \frac{8 M \lambda}{\rho_s L} (\overline{T_1 - T}) \tau \quad (30)$$

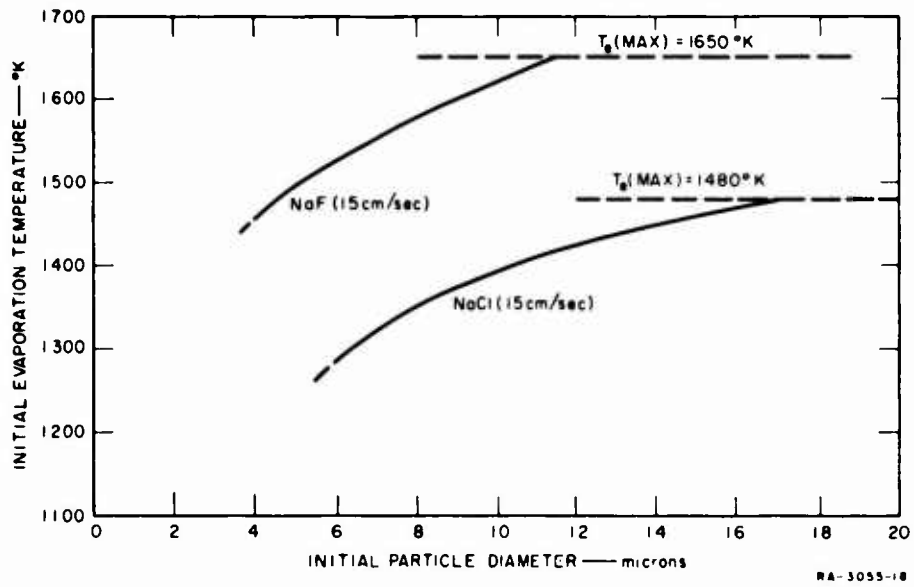


FIG. 16
 INITIAL EVAPORATION TEMPERATURE FOR NaCl AND NaF
 AS A FUNCTION OF PARTICLE SIZE

where

$$d_w = \text{diameter of the particle at } x = \delta$$

$$(\overline{T_1 - T}) = \text{the average temperature difference between the gas and the particle in the interval } \delta - x_e .$$

Further, $\bar{v} = 4S$, and after substitution for τ and \bar{v} and some manipulation, Eq. 30 can be transformed into Eq. 31, a form suitable for determining the degree of evaporation.

$$\frac{d_w^2}{d_0^2} = 1 - \frac{2 M c_s (\Phi\delta)_0}{3 L} \left(1 - \frac{x_e}{\delta}\right) (\overline{T_1 - T}) \quad (31)$$

The double parameter $(\Phi\delta)_0$ is the value of $\Phi\delta$ appropriate to d_0 and to an assumed value of the flame speed. The quantity $1 - \frac{x_e}{\delta}$ can be obtained from a graph of $(T_1 - T_e)_1$ as a function of $(\Phi\delta)_0$, the δ value of $(\Phi\delta)_0$, and Eq. 12. The quantity $(\overline{T_1 - T})$ may be taken without significant error as the average of $(T_1 - T_e)_1$ at $x = x_e$ and $(T_1 - T_e)_f$ at $x = \delta$. For NaCl, $(T_1 - T_e)_f = 720^\circ\text{K}$ and for NaF, $(T_1 - T_e)_f = 550^\circ\text{K}$.

So, proceeding as indicated, we calculated the fractional degree of evaporation, $f = 1 - \frac{d_w}{d_0}$, for NaCl and NaF. The results are shown in Fig. 17. The product Sd_0 is constant for a given degree of evaporation. Consequently, the variation of f with particle size for any flame speed can be easily obtained once the variation is known for a single flame speed.

The calculation of degree of evaporation carried out for $x = \delta$ can be done for other selected values of x . For the purpose of demonstrating that small particles of materials such as NaCl and NaF will partially evaporate during passage through a flame, the results shown in Fig. 17 for $x = \delta$ are sufficient.

The mathematical analysis just described can only be successfully applied to materials for which there is available a relation between the vapor pressure and the temperature of the material. Substances such as Na_2CO_3 , which decompose during evaporation cannot be treated. Therefore, the relative volatility of several such materials was determined in the following way. A small quantity of material was fused by flame onto the end of a platinum wire until a small bead about 1 mm in diameter had been formed. The bead and wire were suspended in a Meker burner flame about 1 cm above the primary cones. By stopwatch the time was measured from the appearance of color in the flame gases to the disappearance of that color. The reciprocal of the bead lifetime was taken as a measure of the volatility of the test material. The results of such measurements are shown in Table V.

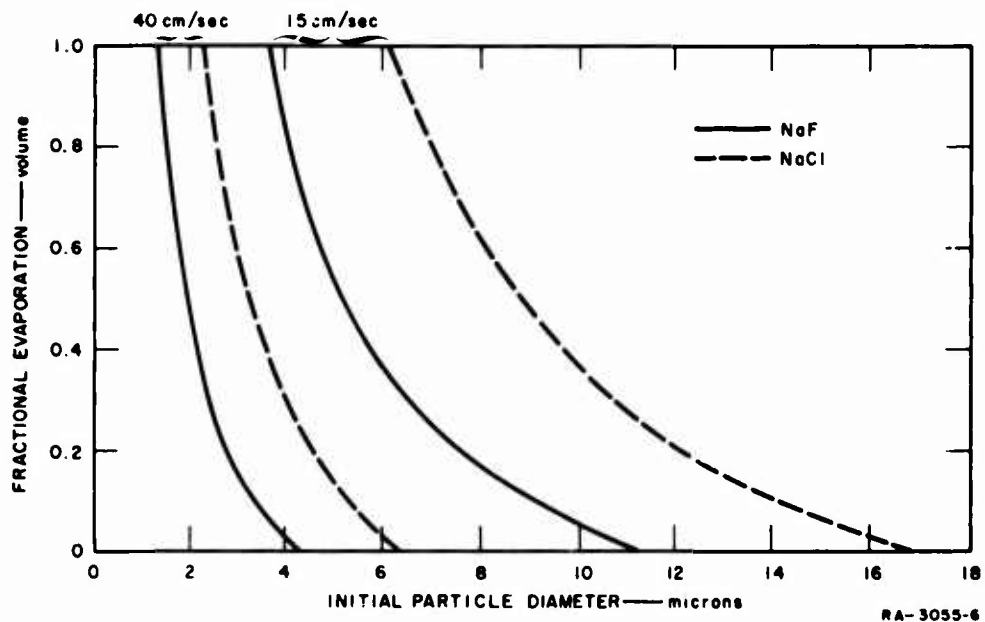


FIG. 17
 FRACTIONAL EVAPORATION OF NaCl AND OF NaF ON LEAVING THE REACTION ZONE

Table V
RELATIVE VOLATILITY OF VARIOUS SOLIDS

<u>Substance</u>	<u>τ (sec)</u>	<u>B.P. ($^{\circ}$K)</u>
NaI	~ 1	1577
KCl	~ 2	1680
CuCl	~ 2	1639
NaBr	~ 2	1666
NaCl	3	1738
K ₂ CO ₃	7
K ₂ SO ₄	10
Li ₂ CO ₃	11
NaF	13	1977
Na ₂ CO ₃	16

τ = lifetime of 1 mm bead of material when exposed to a Meker flame

Table VI
THE PRODUCT OF SPECIFIC HEAT AND DENSITY FOR VARIOUS SALTS

<u>Substance</u>	<u>c</u>	<u>ρ</u>	<u>cρ</u>
K ₂ SO ₄	0.184	2.66	0.49
CaF ₂	0.211	3.18	0.67
KCl	0.154	1.98	0.31
NaCl	0.208	2.17	0.45
Na ₂ CO ₃	0.252	2.51	0.63
NaF	0.27	2.6	0.7
NaBr	0.121	3.2	0.39
CuCl	0.097	3.53	0.34

c = specific heat (cal gm)

ρ = density (gm cc)

Consideration of the data in Table V reveals a number of interesting facts. NaF and Na₂CO₃ have roughly the same volatility. Consequently, the degree of evaporation derived for NaF and shown in Fig. 17 can be expected to apply roughly to Na₂CO₃ as well. Next, K₂CO₃ is seen to be about twice as volatile as Na₂CO₃. This is also about the same as the ratio of inhibition effectiveness for these two materials. Lastly, all the test substances except Na₂CO₃ are more volatile than NaF and small particles of these substances would be expected to evaporate during passage through a flame to an even greater extent than NaF particles of the same size. Powders of all but two of the materials listed in Table V were tested experimentally and found to be effective inhibitors of CH₄-air combustion. Materials which were not effective inhibitors -- talc, CaCO₃, Ca(OH)₂, and CaF₂ -- are not volatile even at flame temperatures and would not be expected to evaporate to a significant extent during passage through a CH₄-air flame, although CaCO₃ and Ca(OH)₂ might decompose to CaO. It appears that evaporation and inhibition effectiveness are companions and that the observed inhibition is due to evaporated materials.

The parameter ϕ defined in Eq. 16 depends on the product $c_s \rho_s$ and, therefore, will vary from substance to substance. As with the other physical quantities used in this analysis, the appropriate values are averaged over the temperature range of interest. The range of values which might be encountered is probably comparable with the range of values at room temperature. As shown in Table VI there is only about a factor of two between the lowest and highest values. The effect of averaging with respect to temperature is not great. The room temperature product $c_s \rho_s$ for NaCl is 0.45, while the average value, even though it includes the heat of fusion, is only about 0.67.

IV DISCUSSION

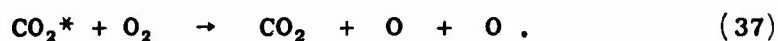
A. Inhibition by Volatile Compounds

The inhibition of hydrocarbon combustion by halogen compounds volatile at room temperature appears to involve at least two different mechanisms. These mechanisms are not mutually exclusive and may occur together under appropriate circumstances. The first of these mechanisms we proposed (Ref. 10) to account for inhibition by such substances as Br₂, HBr, CH₃Br, CH₃I, etc. The important halogen species involved in this mechanism are the halogen atoms X and the halogen acids HX. The reactions associated with inhibition may be formally represented by



The species H α may be any molecules containing hydrogen which can be abstracted by X. In particular, H α may be the fuel. The species β may also be any one of a large number of molecules. The important β are the species H, O, and OH which are reaction intermediates during combustion.

The removal of these species decreases the overall rate of reaction because of the importance of such reactions as



The sensitivity of hydrocarbon combustion to inhibition by halogen compounds probably reflects the fact that reaction 35 and the reaction pair 36, 37 are chain-branching reactions. Removal of radicals involved in chain-branching reactions is an efficient way of reducing chain length and average reaction rate. Experimentally it has been found that reaction 35 is a major route for O_2 consumption during hydrocarbon combustion (Ref. 11). Reactions 34 and 36 undoubtedly occur inasmuch as the necessary reactants are present in the flame. The large activation energy associated with reaction 35 is one reason why increasing flame temperature decreases the ability of HBr to quench hydrocarbon flames (Fig. 2). The competing inhibition reaction



has little activation energy. Consequently, an increase in temperature will favor reaction 35 over reaction 38.

The mechanism represented by Eqs. 32 and 33 can be expected to occur whenever halogen compounds are present in the flame. By decomposition or reaction the original additive can provide halogen atoms or halogen acids which then react as indicated. Most of the observed effectiveness of such compounds as BBr_3 can be attributed to the three Br atoms in the molecule.

If the halogen compound is sufficiently stable with respect to decomposition, the original compound added to the unburned mixture can survive as an entity into the reaction zone of the flame and be available for reaction. The two phosphorous compounds PCl_3 and POCl_3 are probably in this category. Reactions such as



could take place in the flame and result in a significant degree of inhibition for reasons already cited. A number of other chlorine compounds of comparable effectiveness (Ref. 12) may function in the same way. The compound BBr_3 may also, although the product HBr is itself chemically active and will contribute to the overall effectiveness of the compound. The HCl formed in Eq. 39 can itself inhibit combustion, but the observed effectiveness is far greater than can be accounted for by the HCl resulting from reaction of PCl_3 or POCl_3 .

For phosphorous-containing compounds some additional mechanism of inhibition must also be involved. Both $(\text{CH}_3)_3\text{PO}_4$ and $(\text{C}_2\text{H}_5)_3\text{PO}_4$ are

strong inhibitors of hexane-air flames (Ref. 12). It is unlikely that inhibition of the degree observed is associated with the organic groups. The phosphorous products in combustion are most likely oxides or hydroxides. In the course of forming such products, the phosphorous may remove reaction intermediates. Additional work is required to elucidate the mechanism.

B. Inhibition by Powders

The theoretical analysis presented in Section III revealed that a significant amount of evaporation will occur for those powders which were found to be effective inhibitors. The extent of evaporation will depend on the temperature history of the powder particles and on the volatility of the material. The calculated results for NaCl and NaF shown in Fig. 17 indicate a high degree of evaporation by the end of the reaction zone. The average extent of evaporation in the reaction zone will be lower. For all but the very finest powders the degree of evaporation for the spectrum of particle sizes present in the powder is probably much less than one. Under such conditions one would expect a proportionality between powder effectiveness and specific surface area. An increase in specific surface area will result in greater fractional evaporation. Evaporation can be completed in the post flame gases, but we are not concerned with that region -- only with the reaction zone itself.

Two essential tasks remain: to identify the species responsible for inhibition and the reactions involved. To that end, consider first the relatively simple case of NaCl. The condensed material will evaporate at high temperatures primarily as NaCl molecules. The NaCl in diffusing through the hot reaction gases may be converted to Na by reactions such as



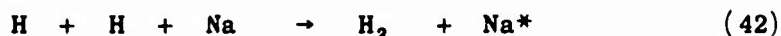
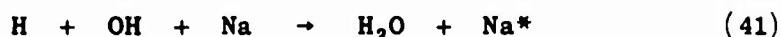
Experimental observation of flames in which Na and Cl were both present indicates that the conversion will not be complete (Ref. 13). Consequently, both Na and NaCl must be accepted as major species involving Na. Traces of NaOH can also be present, as well as minute concentrations of sodium hydride or sodium oxides. However, the oxides have never been observed spectroscopically in flames which also contained sodium (Ref. 14). Inasmuch as only minute concentrations are required to give observable emission spectra, the presence of significant quantities of these compounds is unlikely. As far as NaCl is concerned, the major species to consider are Na and NaCl.

Consider next the more complicated case of Na_2CO_3 , which evaporates with decomposition. Depending on the circumstances one may initially have Na, Na_2O , Na_2O_2 , etc. The initial spectrum of products in the course of diffusing away from the particle will be altered. The major species to be expected at some distance from the particle is the Na atom. The presence of chlorine species in the gas will convert a portion of that sodium into NaCl. The observed decrease in powder effectiveness (see Fig. 13) indicates that NaCl is relatively inactive and that inhibition is associated with the

sodium atom. By implication the overall effectiveness of a sodium compound depends not only on volatility but also on the availability of the atom after evaporation. By analogy other alkali metal compounds would behave similarly. The ability to inhibit combustion is probably not limited to the alkali metal atoms in view of the similar results obtained with NaCl and CuCl: The two are of comparable volatility and both would yield some metal atoms, Na in the one case and Cu in the other. Further, both $\text{Pb}(\text{C}_2\text{H}_5)_4$ and $\text{Fe}(\text{CO})_5$ strongly inhibit hexane-air flames (Ref. 12). A metal atom mechanism may be operative in those cases too, although both Fe and Pb may be partially converted to oxides or hydroxides.

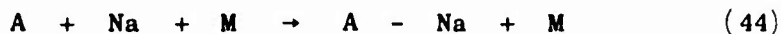
The second task is to identify a mechanism of inhibition which depends on the presence of metal atoms. A number of possible mechanisms were considered. Of these, three were found to be consistent with the obtained results.

It is possible that metal atoms increase the rate of recombination of the radicals directly associated with flame propagation -- H, O, and OH. Recombination reactions limit the concentration of radicals in the flame and insure their removal in the post flame gases. Consequently, an increase in recombination rate can be expected to reduce flame speed. A metal such as Na, which we will use as an example, can affect recombination rate by acting as a third body which is efficient in absorbing a portion of the energy of recombination.



The efficiency of Na as a third body in reactions 41 and 42 has been measured in flame gases (Ref. 15) but is not greater than that of other flame components present in far larger amounts. Therefore, little direct effect can be expected. However, Na does remove at least 50 kcal of energy, the excitation energy for the transition $\text{Na}(^2\text{S}) \rightarrow \text{Na}^*(^2\text{P})$. This excitation energy may then be radiated as light or degraded into heat by collision with other molecules. On the other hand, such third bodies as the product molecules H_2O , H_2 , or O_2 may absorb all or a portion of the energy released in recombination reactions of the type shown in Eqs. 41, 42, and 43. Such molecules with excess energy may be unusually reactive. However, in the case of vibrationally excited product molecules collisions with other molecules will lead to rapid loss of this energy. The mechanism cited cannot be definitely ruled out on the basis of our present knowledge about the state of excitation of the products resulting from recombination reactions.

A metal such as Na can also alter a rate of recombination by a two-step process like that shown formally in Eqs. 44 and 45.



in which A and B are H, O, and OH, and M is a third body. The first product Na-A need not be a major species but it must be sufficiently stable to exist for long enough to react with B. If the product molecule Na-A does survive this length of time and if reaction 45 is exothermic, the rate of reactions 44-45 relative to the direct recombination



will be about equal to the ratio Na/B. In order to evaluate the feasibility of this mechanism the cited ratio must accordingly be known.

The equilibrium concentrations of H, OH, O in the post flame gases of a one-atmosphere stoichiometric CH₄-air flame are known (Ref. 16).

$$T_a = 2214^{\circ}\text{K}$$

$$\text{Equilibrium Mole Fractions} \quad \left\{ \begin{array}{l} \text{H} = 3.57 \times 10^{-4} \\ \text{OH} = 27.8 \times 10^{-4} \\ \text{O} = 2.11 \times 10^{-4} \end{array} \right.$$

In the flame zone itself the concentrations of these three species are undoubtedly much higher. The cited values are only lower limits. The concentration of Na in an inhibited flame can be estimated from the data shown in Fig. 7 for fine Na₂CO₃. About 0.003 mg/cc reduces propagation velocity by about half of the original value. The mole fraction of Na corresponding to that concentration is about 1.5 x 10⁻³. If the average degree of evaporation in the flame is about 10%, the mole fraction of Na in the gas will be 1.5 x 10⁻⁴. A higher degree of evaporation is unlikely in view of the proportionality between specific surface area and powder effectiveness. Comparison of the mole fraction of Na in the flame with the lower limit values for H, OH, and O indicates that the ratio Na/B in the flame is probably much less than one. In the post flame gases, the degree of evaporation is much higher and the concentration of radicals lower. In that region the mechanism is a feasible one, although it is apparently not feasible in the reaction zone unless the estimates of concentration are badly in error.

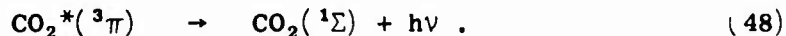
Finally, Na may deactivate energetically excited species like O₂*, CO₂*, C₂*, CH*, OH* or other species not listed. The concentration in the flame of each of the cited species is not known but is probably low. These species may in addition be sideshow performers not directly involved in flame propagation. Consider for instance C₂* and CH*. Emission intensities from C₂* and CH* increase with the addition of bromine inhibitors (Ref. 10), although flame speed decreases. Both C₂* and CH* are apparently unrelated to flame speed. On the other hand, emission intensity of OH* decreases with increasing concentration of bromine inhibitor (Ref. 10). However, OH* is de-excited on virtually every collision with flame gases (Ref. 17). Consequently, a minor constituent can have little further influence on the deactivation of OH*. The decrease in emission intensity is probably associated with a diminution in the rate of production of OH*

upon the addition of an inhibitor. Our previous conclusion (Ref. 10) that OH* is removed by reaction with HBr is apparently wrong.

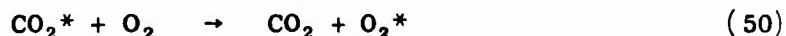
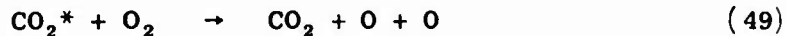
Inhibition can result from the deactivation of CO₂*. The reactants necessary to form CO₂* are present in the flame, such as



Moreover, CO₂* is metastable with respect to radiation because of the multiplicity-change associated with the radiative transition (Ref. 18),

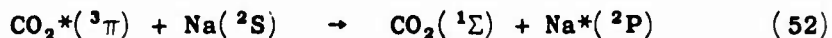


Excited CO₂* can therefore exist for a time and be available for reactions such as those shown (Ref. 18)



Oxygen atoms produced by reactions 49 and 51 may by further reaction produce H and OH. Reactions 34 and 35 are still important but would depend on the rate of reaction 47.

If Na (or other metal atom) is present in the flame the de-excitation reaction



could remove the energy required for reaction 49. The excitation energy of Na*(²P) may be radiated or eventually degraded into thermal energy by collision. The excited O₂* formed in reaction 50 can also lose its energy of excitation by collision with Na, especially if the O₂ is only vibrationally excited (Ref. 19). This mechanism of inhibition, the removal of excitation energy by metal atoms, provides a qualitative explanation for metal inhibition. So far as known, it is consistent with fact. The mechanism does require that CO₂* be a featured performer in the combustion of hydrocarbons.

V CONCLUSIONS AND RECOMMENDATIONS

A. Inhibition by Volatile Compounds

A great number of volatile halogen-containing compounds are now known to be combustion inhibitors. These include the compounds discussed in this report as well as a number of other (Refs. 10, 12). There seems to be little reason to add to an already long list until greater understanding of the pertinent chemistry has been acquired. It seems more appropriate now to explore in detail the inhibition mechanism for selected inhibitors such as PCl₃. To establish an inhibition mechanism the combustion mechanism itself must be established and experimentation directed to that end

would be as valuable as studies directly concerned with inhibition. The use of inhibitors may provide a means of investigating the combustion mechanism. For example, it was the sensitivity of hydrocarbon flames to the presence of bromine compounds that led us to the conclusion that chain-branching is an important feature of hydrocarbon flames. Equally pertinent are theoretical and experimental studies of the phenomena involved in the extinction of both diffusion and premixed flames.

B. Inhibition by Powders

It has already been noted that the overall effectiveness of a finely dispersed powder depends mainly on four factors: (a) the extent of powder evaporation, (b) the degree to which the evaporated material results in the formation of metal atoms, (c) the effectiveness of the metal atom, and (d) the inherent sensitivity of the combustion system to inhibition of this type. For hydrocarbon-air combustion, factors (a) and (b) are the most important and will largely determine the overall effectiveness of the material.

The processes which affect the degree of evaporation have been discussed in Section III. The two most important limitations on evaporation are the inherent volatility of the material and the fineness of the powder. The smaller the particle size, the more rapidly the particles will be heated to a temperature at which evaporation can proceed. From the standpoint of volatility the alkali halides would make excellent inhibitors; but not all the alkali metal atoms are chemically available inasmuch as a substantial portion of the evaporated material exists as alkali-halide molecules. A similar situation can exist if the metal atom forms hydroxides or oxides stable in a flame. Accordingly, in evaluating the possible usefulness of a material, both volatility and metal availability in the flame must be considered. The third factor, difference in effectiveness from one kind of metal to another, is not known. Inhibition effectiveness is not limited to the alkali metals, but it is not known whether all metals or only a few possess the ability to inhibit hydrocarbon combustion (cf. Ref. 15). The final factor, the sensitivity of the system, is not a controllable variable. A large degree of sensitivity is to be expected for all those systems in which the fuel is a hydrocarbon, or a hydrocarbon derivative, and the oxidizer is O_2 . However, one may conclude that such flame systems as CH_4-NO_2 will not be sensitive to inhibition by powders. A CH_4-NO_2 flame is not hot enough to evaporate materials such as Na_2CO_3 . A necessary condition for sensitivity to chemical inhibition is the existence of long reaction chains. A useful criterion in deciding whether chains are important is the flame speed of the premixed flame. For example, a CH_4-NO flame which is hot but relatively slow burning probably does not involve long chains and by that criterion would not be sensitive to chemical inhibition (see p. 100, Ref. 1).

One of the most important aspects for future study is the detailed mechanism by which metal atoms inhibit combustion. On a molar concentration

basis the effectiveness of certain metal atoms is greater than that of other known inhibitors. It is not known whether this is a general property of metal atoms or is limited to relatively few. Studies related to any of the four factors cited above would be pertinent. Specific items might include:

- (a) The sensitivity to metal atom inhibition of premixed flames which are unusual in some way, such as: (1) CH_2O -air flames which normally produce very little ionization or abnormal excitation of metal atoms when the atoms are present in the flame, or (2) the NH_3 -air system which offers different types of intermediates during combustion
- (b) Spectroscopic studies (emission and absorption) of premixed hydrocarbon- O_2 -diluent flames to which small quantities of metal atoms have been added
- (c) The decomposition and evaporation of materials such as Na_2CO_3 which are known to inhibit combustion
- (d) Studies of the phenomena leading to extinction of both premixed and diffusion flames; in this regard, it should be noted that the flame speed of a premixed CH_4 -air flame is affected more strongly by Na_2CO_3 powder than is quenching distance; the origin of this difference may lie in the large temperature coefficient associated with evaporation of powder materials; additional work is required to elucidate the details of the mechanism
- (e) Studies of the limitations and advantages associated with the use of nonvolatile materials which nevertheless must evaporate in order to be effective.

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