Mechanical Engineering
Report ME-RT 70009

Final Summary Report
on
THE INVESTIGATION OF FLAME SPREADING OVER THE SURFACE OF IGNITING SOLID PROPELLANTS

by

Richard S. Magee
Robert F. McAlevy III

MARCH 31, 1971

Approved by: Richard S. Magee
Richard S. Magee
Co-Principal Investigator

Robert F. McAlevy III
Robert F. McAlevy III
Co-Principal Investigator

FACILITY FORM 602

N71-31426	N71-31431
(ACCESSION NUMBER)	(THRU)
74	G3
(PAGES)	(CODE)
CR-111942	33
(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
OFFICE OF SPACE SCIENCE AND APPLICATIONS
Washington 25, D. C.

Grant No. NGR-31-003-014

STEVENS INSTITUTE OF TECHNOLOGY
DEPARTMENT OF MECHANICAL ENGINEERING
CASTLE POINT STATION
HOBOKEN, NEW JERSEY 07030

PROLOGUE

This document comprises the Final Summary Report on "The Investigation of Flame Spreading Over the Surface of Igniting Solid Propellants", sponsored by NASA Grant No. NGR-31-003-014 and conducted in the Combustion Laboratory at Stevens Institute of Technology.

Some of the information presented herein (i.e., Part III, Part IV, and Part V) has been reported previously in Annual Reports distributed according to NASA specifications during the term of the Grant. It has been included for completeness in the form published in the archive technical literature.

Part II contains information that has not been reported previously, but will appear in the Proceedings of the Thirteenth International Symposium on Combustion to be published later this year.

Part I contains information that has also not been reported previously and has not as yet been submitted for publication.

As reported in Parts II through V, a wide variety of materials exhibit flame-spreading characteristics in oxygen-containing quiescent environments that can be correlated by the now well-known power-law:

$$V \alpha (PY_{ox}^{m})^{\Phi}$$

where: V is the flame spreading velocity

P is the environmental pressure

Y_{ox} is the gas-phase reactive component mole fraction.

This finding has been rationalized, and is available as the basis for design of practical solid propellant rocket motor ignition systems as well as the basis for minimization of the flammability hazard in space-capsule environments.

An unexpected finding is reported in Part I: The ICRPG Standard Reference Composite Propellant does not follow this power-law. In fact, above a certain threshold pressure level, increasing the pressure decreases the flame spreading velocity! If such behavior is common to practical composite propellants, then current ignition system design criterion will have to be modified to account for this behavior. Unfortunately, time did not permit testing of other composite propellants.

The flame spreading information developed during this program can be utilized to minimize the flammability hazards of cellulosic and polymeric fabrics and structural materials. And thus represents an aerospace information "fallout" that is of societal benefit.

Table of Contents

Page

Part I:

Part II:

Part III:

Part IV:

Part V:

PART I

AN INVESTIGATION OF THE FLAME SPREADING CHARACTERISTICS OF THE ICRPG STANDARD REFERENCE COMPOSITE PROPELLANT AND ITS CONSTITUENTS

The contents of PART I of this report have been submitted by Kenneth S. Pope in partial fulfillment of the requirements of the degree of MASTER OF ENGINEERING (MECHANICAL) from Stevens Institute of Technology June 1971

ABSTRACT

This work describes an experimental investigation of the surface flame spreading characteristics of the ICRPG reference composite propellant, composed of ammonium perchlorate (76% by wt.) in a matrix of polyurethane binder (24% by wt.). Tests were conducted on both the propellant and its constituents in a pressure vessel, under quiescent conditions, to determine the dependence of the flame spreading velocity on environmental composition and pressure.

Small specimens were mounted horizontally in a chamber and ignited by an electrically heated wire placed at one end. The dimensions of the test enclosure were such as to minimize combustion-induced flow and thereby minimize problems associated with convective flow in the environment.

Flame spreading velocities over the propellant were measured in methane, and in oxygen-nitrogen mixtures, with oxygen mole fraction, Y_{ox}, of 0, 0.21, 0.40, 0.65, and 1.0. Environmental pressure (P) was varied between 4 and 415 psia. In the O_2/N_2 environments below 150 psia, the flame spreading velocity (V) was found to follow the familiar power-law relation previously exhibited by a wide variety of other materials, $V\alpha(PY_{ox}^{m})^{\Phi}$. However, whereas all other materials exhibited $m>1$ and $\Phi<1$, the ICRPG propellant exhibited $m=0.65$ and $\Phi=1.2$.

A further departure from past experience was observed at $P>150$ psia - Φ decreased with increasing P. At 200 psia or so $\Phi\simeq 0$, and for $P>200$, $\Phi<0$. That is, increasing P resulted in decreasing V. This had never been observed with any material in the past.

In a pure N_2 environment, although peaking also occurred at about 150 psia, the flame spreading characteristics of the propellant could not be represented by a power-law of the form $V \alpha P^{\Phi}$ below this pressure. In addition, the flame spreading velocities of the propellant measured in methane were virtually identical to those obtained in nitrogen! This suggests that, in the absence of oxidizing species in the gas phase that can react with the binder pyrolysis products, the flame spreading characteristics are independent of environmental composition.

The propellant surface regression rate during normal deflagration (r) was measured as a function of P in air. The r(P) data exhibited a "plateau" at 500 psia or so, but in general was so different from the flame spreading data that the two could not be correlated.

The ICRPG binder was tested in environments containing mixtures of oxygen and nitrogen at the same conditions used in the propellant experiments. Results of the binder tests could also be correlated by $V \alpha (PY_{ox}^{m})^{\Phi}$, but with $m=2.7$ and $\Phi=0.75$. Pressed ammonium perchlorate specimens were tested in methane over the same pressure range and the data was correlated by $V \alpha P^{\Phi}$, with $\Phi=0.75$. Thus, the propellant constituents tested separately exhibited different characteristics than the propellant itself, i.e., no peaking of V(P) data, and power-law exponents typical of those found with all other materials tested in the past.

It is concluded that the ICRPG propellant flame spreading characteristics cannot directly be related to those of its constituents at this time; but that these characteristics must be studied with the propellant itself.

List of Figures

BACKGROUND AND INTRODUCTION

Solid propellant rocket motor ignition systems are developed according to certain empirical, and not always reliable, guidelines that have been evolved over the years. This approach is costly, both in time and money, and it frequently proves to be only marginally successful -- a result of a series of "fixes", rather than a logical answer to the particular need. It has been hoped for the last few years now that some rational basis for the design of the ignition system could be established. However, this has been prevented by a lack of knowledge of the mechanism by which the propellant grain responds to the igniter stimuli--that is, how motor ignition actually takes place.

Almost every type of currently operational igniter acts by heating exposed surfaces of the propellant grain, the source of energy being the hot products produced by combustion of the igniter materials. The overall motor ignition process, following igniter firing, can be thought of most conveniently as being composed of three principal phases:

(1) heating of the exposed grain surface to incipient ignition conditions, and the actual development of ignition at some location,

(2) spreading of the flame over the remainder of the surface, and finally,

(3) filling of the chamber with propellant combustion products until the equilibrium chamber pressure is reached. If the igniter continues to fire during the flame spreading and chamber filling phases, its effect would have to be accounted for in a valid theoretical description of the overall motor ignition process.

The first phase has been receiving a good deal of attention during the last decade and has been the subject of extensive research (Ref. 16). The final phase can be described very accurately on the basis of a straightforward balance between the rate at which gas is being generated in the motor and the rate at which it is being expelled (Ref. 17). Only recently has the mechanism underlying the second phase, that is, flame spreading, been subjected to detailed investigation (Ref. 1, 2, 4, 8).

While this portion of the ignition transient in small motors may occur within a few milliseconds, the geometry of larger space booster motors can extend this interval to about one second. Therefore, this lag can become quite vital in cases such as motor clustering where exact firing schedules are required. In fact, with solid propellant and hybrid rocket motors alike, full power is not achieved until flame spreading and pressure buildup is completed.

A better understanding of the flame spreading process must be achieved and incorporated in the numerous theoretical approaches dealing with the overall ignition process. Boundary conditions involving the flame spreading phase have been treated rather unrealistically in the various integration schemes set forth to date (Ref. 9, 10, 11). The most commonly misused boundary condition is the "ignition temperature" criteria associated with the questionable "solid phase" ignition theory (Ref. 5). Another such erroneous scheme proposes the existance of a linear relationship between burning rate and flame spreading rate (Ref. 9).

In its most general form, a complete description of flame spreading must include the dominant effects of environmental composition, pressure, and flow velocity. This last factor, however, brings to bear the additional complexity of forced convection, which will not be dealt with in this study. The present lack of knowledge with regard to the processes involved in flame spreading necessitates limitation of experimental variables so as not to obscure the underlying nature of the mechanism. Nevertheless, the simplified problem is both realistic and practical. For example, the use of aft-end igniters in large rocket motors results in a stagnation region where the effects of convective flow are negligible. Even for the case of high penetration encountered with a supersonic igniter, as much as 20 to 30% of the propellant surface will be in the stagnation region (Ref. 3).

To date, much information has been obtained for flame spreading over solid propellants and propellant constituents in quiescent environments (Ref. 1, 2, 4, 8). Previous studies, however, deal either with homogeneous nitrate esther propellants or the individual constituents of heterogeneous (or composite) propellants. No detailed investigations have been made of the flame spreading characteristics of a specific composite propellant, and its constituents, under quiescent conditions. Flame spreading characteristics of their fuel and oxidizing constituents may be examined individually, and hopefully aid in a better understanding of the propellant itself. This was done during the subject program.

For ease of standarization, and ready accessability, the ICRPG reference composite propellant was chosen for study. It is composed of an ammonium perchlorate oxidizer (76% by wt.) in a polyurethane binder (24% by wt.). Flame spreading characteristics of both the propellant and its ingredients were studied with respect to variations in pressure and environmental composition.

DISCUSSION OF THEORY

The flame spreading phenomenon is looked upon in this work as a continuous gas phase ignition process, as proposed by McAlevy and Magee (Ref. 2). From this viewpoint one can conceptualize the moving flame as a source of heat by which the elements before it are raised to their vaporization temperature. Specifically, one may characterize the events taking place in flame spreading as: heating of the surface before the flame; vaporization; diffusion and mixing with gaseous reactants; and finally, ignition and combustion of the resulting gaseous mixture. This theory is enforced by studies from this laboratory (Ref. 1, 2).

It can be seen that such a sequence closely links flame spreading to the basic ignition process. The latter presents itself as a somewhat more simplified problem to treat analytically since it is merely a single phase of flame spreading. However, despite the comparative analytical complexity of flame spreading, it lends itself more easily to experimental investigations than ignition studies do. Ignition studies tend to show a great deal of dependency on experimental procedure, due to the variations in surface heating and ignition criteria employed by the different researchers. Flame spreading, on the other hand, provides its own heat source (the advancing flame) and an inherent ignition criteria (arrival at a point of interest of the well-defined flame front).

An approximate solution for the gas phase ignition theory of flame spreading has been set forth by McAlevy and Magee (Ref. 2). The resulting relationship shows a power-law dependency of flame spreading velocity on pressure (P) and oxygen component mole fraction (Y_{ox}). Although the basic equation ($V \alpha (PY_{ox}{}^{m})^{\Phi}$) is derived for the case of a single component solid phase material, it has been postulated that it can also adequately describe the behavior of materials with two reactive components in the solid phase (Ref. 2). Therefore, an attempt will be made to employ this relation to correlate data obtained for both the propellant and its ingredients.

EXPERIMENTAL

I. Flame Spreading Velocities

The flame spreading velocity over the surface of the ICRPG reference composite propellant and its ingredients was measured in quiescent environments under pressures varying from 4 to 415 psia. Tests on the propellant were conducted using methane and mixtures of oxygen and nitrogen as the gas phase environment. Oxygen mole fractions used for the O_2/N_2 mixtures were 0,0.21, 0.40, 0.65, and 1.0. The polyurethane binder was only tested in O_2/N_2 mixtures however, while the ammonium perchlorate oxidizer was only tested in methane.

A. Sample Preparation

Small test specimens (3in. x 0.375in. x .125in.) were mounted horizontally on backing plates, with the 3in. x 0.375in. surface upwards. The techniques employed for preparing samples of each material are discussed below.

1. Polyurethane Binder

Test specimens were fastened to asbestos backing plates using Sauereisen Insa-Lute Adhesive Cement No. 1 paste. To prevent the flame from spreading too rapidly along the 3in. edges of the specimen--a phenomenon that takes place faster than flame spreading over the top surface, and therefore one that could result in spurously higher measured values of the flame spread rate--it was necessary to inhibit the edges of the specimens. This procedure involved coating the sides and a 1/32" overlap along the 3" edges of the top with Sauereisen Cement.

2. ICRPG propellant

Sauereisen could not be used for inhibition and mounting of the propellant since it tended to penetrate too deeply into the relatively porous surface. This problem was overcome by using asbestos paper bonded to the surface with Borden's Elmer's Glue-All, which is designed for use on porous surfaces. Microscopic examination showed that this procedure resulted in negligible penetration of the inhibitor into the test sample.

3. Ammonium perchlorate oxidizer

Ammonium perchlorate samples were formed by pressing AP granules in a mold with a hydraulic press at 20,000 psig. These samples were then inhibited by manually pressing each one into an asbestos jig lined with Johns Mansville's Duxseal, a packing clay. The clay extended onto the top surface 1/32" along the 3" edges. Although the ammonium perchlorate used had approximately the same granualarity (177μ-208μ) as that used in the ICRPG reference propellant (200μ), this technique resulted in a mirror-like finish of the pressed specimens. While this minimized any surface roughness effects, which could intensify radiant heat flux at certain locations, the surface was quite different than in the actual propellant, where the projection of AP particles above the binder resulted in a fairly rough texture.

B. Test Apparatus

The test apparatus consisted of a test chamber, "surge" tank, vacuum pump, gas supply, air compressor, cinecamera, as well as valving, piping and wiring. A schematic arrangement is shown in Figure 1.

The samples were burned in a relatively large test chamber (10in. i.d. x 18in.) fitted with an observation window. Pressure increase in the chamber during flame spreading was reduced to a negligible level by connecting a large surge tank (10 cu. ft.) to the test chamber. A "one-way" valve was inserted between the chamber and the surge tank. In preparing an experimental run at a selected pressure, the surge tank was first pressurized to that level with compressed air (Note: N_2 was used instead of air for runs using 100% methane). After placing a mounted specimen in the chamber, it was sealed and evacuated. The chamber was then charged with the selected test gas to the pressure in the surge tank, thus opening the check valve.

The chamber gas was allowed to reach a quiescent state before igniting the specimen by means of an electrically heated wire previously positioned along the 0.375in. edge on the top surface.

C. Flame Spreading Velocity Measurement

Flame spreading data were obtained for high spreading velocities from cinecamera records. Low spreading velocities (below 0.5in/sec.) were determined from stopwatch measurements of the time required for the flame to propagate a fixed distance of 1". For those events which were recorded photographically, Kodak Tri-X 16mm film and a Bell and Howell 16mm Model 70-D1 cinecamera were used. From the developed film, flame spreading velocity was determined using a motion analyzer (Vanguard, Model M-16).

II. Burning Rates

Propellant burning rate measurements were made using essentially the same test procedure and equipment described in Reference 15. The pressure range used was the same as for the flame spreading tests. Since spot checks showed burning rate invarience with oxygen mole fraction, all tests were run in air.

Side inhibition was also needed for the burning rate tests. For this case, ½" dia. x 6" long propellant rods were coated over their entire length with Sauereisen. The samples were then drilled with 3 holes at 2" intervals. Through these were passed timing wires connected to a simple relay and clock circuit. This setup was used to take separate burning rate measurements for each half of the rod.

RESULTS AND CONCLUSIONS

A flame spreading experiment for the ICRPG reference composite propellant and its constituents has been performed in quiescent environments. Flame spreading rates have been measured under various conditions of pressure and chemical reactivity of the surrounding atmosphere. Burning rate measurements for the propellant, over a similar pressure range, have also been made.

The data points, indicated in Figs. 2 thru 9 represent a minimum of 4 test runs each. Limits shown indicate 95% confidence intervals.

PROPELLANT FLAME SPREADING (O_2/N_2, CH_4 environments)

All of the propellant data obtained in O_2/N_2 mixtures are displayed in Fig. 2. These exhibit a peaking of V(P) characteristics at 200 psia or so. This phenomenon had never been previously observed for any combustible material. The peaking starts at about 150 psia, independently of O_2/N_2 composition. At lower pressures the flame velocity shows the familiar power-law dependency, $V\alpha(PY_{ox}{}^{m})^{\Phi}$, with m=.65 and Φ=1.2 (Fig. 3). The values of these power-law characteristics are unique, in that all other materials tested in this or other laboratories (Ref. 14) exhibit values of $\Phi<1$ and values of the product $m\Phi<1$.

In nitrogen however, although peaking also occurred at about 150 psia, the flame spreading characteristics of the propellant could not be represented by a power-law of the form $V\alpha P^{\Phi}$ below this pressure (Fig. 2). The propellant V(P) characteristics in methane were similar to those observed in nitrogen (Fig. 4).

BINDER FLAME SPREADING (O_2/N_2 environments)

The polyurethane binder flame spreading characteristics in O_2/N_2 environments followed the power-law relation throughout the entire pressure range (Fig. 5), with m=2.7 and Φ=0.75. These results are typical of those found for all other combustible materials--excluding the ICRPG propellant.

Reliable data could be obtained only in the regime of V>0.075"/sec. and for O_2/N_2 mixtures with $Y_{ox} \geq 0.40$. For conditions that produced V<0.075"/sec. the binder surface melted and formed a "wave" of liquid polyurethane which preceded the flame front. When this occured, data scatter was very large, since flame propagation became a function of the random structure of this fluid layer. Two distinct patterns were observed: (1) the wave would either spread out horizontally, "dragging" the flame with it; or (2) it would build up vertically, and some of the liquid would flow back into the flame, which would keep the flame essentially stationary. No correlation of wave characteristics and environmental conditions could be found.

When experiments were performed in air $Y_{ox}=0.21$, a great deal of "soot" was formed, which obscured the flame location and prevented determination of V. No soot was observed at $Y_{ox}=0.40$, 0.65 or 1.0.

AP FLAME SPREADING (CH_4 environment)

Flame spreading characteristics of ammonium perchlorate in methane proved to be similar to those of the binder in O_2-inert environments. That is, the data could be correlated by the power-law relation $V \alpha P^{\Phi}$, with $\Phi=0.75$ (Fig. 5).

PROPELLANT DEFLAGRATION RATE (O_2/N_2 environment, $Y_{ox}=0.21$)

The propellant deflagration rate is characterized by a gradual decrease in the dependence of r on P, until at approximately 500 psia it becomes essentially independent of further pressure increase (Fig. 7). Its magnitude is approximately an order of magnitude lower than the propellant's flame spreading velocity. The propellant V(P) characteristics were sufficiently different from the r(P) characteristics that it was not possible to relate the two on any known basis.

COMPARISON OF DATA

Figs. 8 & 9 provide a convenient overview of the combustion characteristics of interest. Before studying these in detail, it is useful to recall the flame spreading characteristics of homogeneous (nitrate ester) propellants previously studied in this laboratory (Ref. 1).

As was found during the current study, the process of flame spreading had no relationship to the process of deflagration. The homogeneous propellant flame spreading characteristics in O_2/N_2 environments could be correlated by the familiar power-law relation ($V \alpha (PY_{ox}{}^{m})^{\Phi}$) with exponents typical of those exhibited by solid fuel-gaseous O_2/N_2 systems. It was concluded that the oxidant vapors arising from propellant decomposition were less powerful than the oxygen in the environment.

The composite propellant flame spreading velocity characteristics in O_2/N_2 environments below 150psia also follow the familiar power-law relation, but with previously unobserved strong P sensitivity (Φ=1.2) and weak Y_{ox} sensivity ($m\Phi$=0.78). This could be rationalized on the basis that the vapors emerging from AP decomposition are more reactive than those emerging from the homogeneous propellant surface. But the peaking characteristics at P greater than 150 psia cannot be easily explained at this time.

The familiar power-law relation and the exponents found with the binder-gaseous oxygen system and the AP-methane system, in contrast to the characteristics found in the propellant -O_2/N_2 system suggests that there is a cooperative effect of the constituents that strongly affects the flame spreading phenomenon in the propellant. The propellant-methane and propellant-nitrogen system characteristics, which are shown to be virtually identical on Fig. 9 and which cannot be correlated by the power-law relation, support the importance of this cooperative effect.

This virtually identical behavior exhibited by the propellant in both the nitrogen and methane environments suggests that, in the absence of oxidizing species in the gas phase that can react with the binder pyrolysis products, the flame spreading characteristics are independent of environmental composition. In this case the processes controlling flame spreading must occur between the binder and solid phase oxidant (AP) pyrolysis products.

The complexity of the cooperative effect is illustrated by the fact that the V for the propellant-methane and propellant-nitrogen system falls below that for the AP-methane system at pressures greater than 400 psia or so (Fig. 8).

Efforts to modify McAlevy and Magee's derivation to include the effects of a heterogeneous mixture of solid fuel and oxidant proved unsuccessful. Both the little known nature of composite propellant deflagration, and the resulting complex three dimensional diffusion problem associated with the composite propellant made an expansion of their analysis beyond the scope of this investigation. Therefore, simplistic speculation concerning the nature of the cooperative effect and its influence on the overall flame spreading mechanism seems inappropriate until a more detailed investigation is conducted.

SUMMARY

The flame spreading characteristics of the ICRPG reference composite propellant and its constituents have been obtained. They were compared with those of its polyurethane binder and its ammonium perchlorate oxidizer. The propellant deflagration rate was also obtained as a function of pressure and compared to the flame spreading characteristics.

The binder flame spreading characteristics were quite similar to those exhibited by a wide variety of other combustible materials. All, for example, show a flame spreading velocity dependence on pressure and oxygen mole fraction of the form $V\alpha(PY_{ox}{}^{m})^{\Phi}$. And all are typified by values of m and Φ very close, or equal, to those of the polyurethane binder (i.e. $m=2.7$, $\Phi=0.75$). This same pressure dependancy ($\Phi=0.75$) was observed for the propellant's ammonium perchlorate oxidizer in methane.

Radically different results were obtained, however, when the product of these two constituents, the propellant itself, was tested. The propellant flame spreading velocity showed a power-law dependancy, ($V\alpha(PY_{ox}{}^{m})^{\Phi}$), within only a limited pressure range ($4<P<150$psia). In this region the values of m and Φ were found to be 0.65 and 1.2, respectively. This high pressure exponent and low oxygen mole fraction exponent are without precedent, and suggest a cooperative effect of the constituents which strongly influences the flame spreading characteristics.

Another previously unobserved characteristic exhibited by the propellant was the maxima behavior. This occured at about 200 psia, and further increases of P resulted in decreasing V. This could be extremely important in practical motor applications. It indicates that if the combustion chamber pressure climbs to

too high a level during the flame spreading phase of the ignition process, it may very well have an effect opposite to that which is usually expected. The ignition transient may actually be prolonged rather than reduced.

Finally, the finding that the flame spreading characteristics of the propellant were virtually identical in both methane and nitrogen environments could be highly significant. It suggests that in the absence of oxidizing species in the igniter gases the flame spreading phase of the ignition transient would be unaffected by variations in igniter gas composition.

REFERENCES

1. McAlevy, R.F. III, Magee, R.S., Wrubel, J.A., Horowitz, F. "Flame Spreading Over the Surface of Igniting Solid Rocket Propellants and Propellant Ingredients", AIAA Paper No 66-68, January.

2. McAlevy, R.F. III, Magee, R.S., "The Mechanism of Flame Spreading Over the Surface of Igniting, Condensed Phase Materials", Twelfth Symposium (International) on Combustion, The Combustion Institute, 1969, p. 215.

3. Kilgroe, J.D., "Studies on Ignition and Flame Propagation of Solid Propellants", Final Report, UTC 2229-FR, United Technology Center, November 1967.

4. Wrubel, J.A., "Flame Spreading Over the Surface of Double Base Propellants at High Pressure", Master's Thesis, Stevens Institute of Technology, Hoboken, New Jersey, June 1966.

5. Price, E.W., Bradley, H.H., Jr., Dehority, G.L. Ibiricu, M.M., "Theory of Ignition of Solid Propellants", AIAA Preprint No. 66-64, 1964.

6. McAlevy R.F. III, Hansel, J.G., "Linear Pyrolysis of Thermoplastics in Chemically Reactive Environments", AIAA J, 3, 2 (1965).

7. McAlevy, R.F. III, Lee, S.Y., Magee, R.S., "The Solid Propellant Ignition Mechanism: A Simple Diagnostic Experiment", Astronaut, Acta, 11, 2, 144 (1965)

8. McAlevy, R.F. III, Magee, R.S., "Flame Spreading at Elevated Pressures Over the Surface of Igniting Solid Propellants and Propellant Ingrediants in Oxygen/Inert Environments", Annual Report ME-RT 67011, October 1967.

9. Bradley, H.H., "Theory of a Homogeneous Model of Rocket Motor Ignition Transients", AIAA Preprint No. 64-127, January 1964.

10. Paul, B.E., Lovine, R., Fong, L.Y., "Propellant Surface Flame Propagation in Rocket Motors", AIAA Preprint No. 64-125, January 1964.

11. DeSoto, S., Friedman, H.A., "Flame Spreading and Ignition Transients in Solid Grain Propellants", AIAA J 3, 405-412 (1965).

12. Lastrina, F.A., Magee, R.S., and McAlevy R.F. III, "Flame Spread Over Fuel Beds: Solid Phase Energy Considerations', Thirteenth Symposium (International) on Combustion, University of Utah, Salt Lake City, Utah, August 1970.

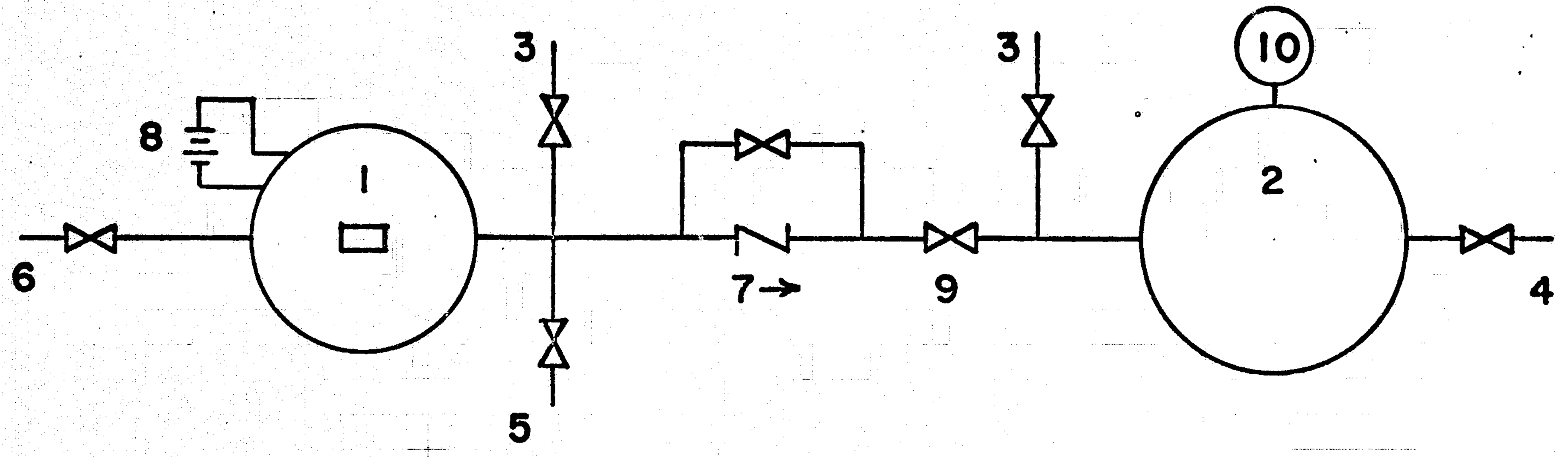
13. McDivitt, J., Naval Ordinance Staiton, Indianhead, Maryland (Private Communication), January, 1969.

14. Friedman, R., "A Survey of Knowledge about Idealized Fire Spread Over Surfaces", Fire Research Abstracts and Reviews, Vol. 10, #1, 1968.

15. McAlevy, R.F. III, et. al.,"Investigation of AP Composite Solid-Propellant Deflagration Mechanism by Means of Experimental Analog Techniques", AIAA J., Vol. 6, No.7, July 1968, pp.1243-1251.

16. Summerfield, M., Shinnar, R., Hermance, C.E., Wenograd, J., "A Critical Review of Recent Research on the Mechanism of Ignition of Solid Rocket Propellants", Aero. Engrg. Report 661, Princeton University, Princeton, New Jersey, August 1963.

17. Parker, K. H., Most, W.J. and Summerfield, M. "The Ignition Transient in Solid Propellant Rocket Motors", AIAA Preprint 66-666 (1966).



1. TEST CHAMBER WITH OBSERVATION WINDOW
2. "SURGE" TANK
3. TO ATMOSPHERE
4. FROM AIR COMPRESSOR
5. TO VACUUM PUMP
6. FROM GAS SUPPLY, PRESSURE REGULATOR, AND PRESSURE GAGES
7. CHECK VALVE (DIRECTION OF FLOW IS INDICATED)
8. IGNITION SYSTEM
9. NORMALLY OPEN VALVE; OTHER VALVES ARE NORMALLY CLOSED
10. "SURGE" TANK PRESSURE GAGE

FIG. I. SCHEMATIC OF APPARATUS FOR FLAME SPREADING VELOCITY MEASUREMENT

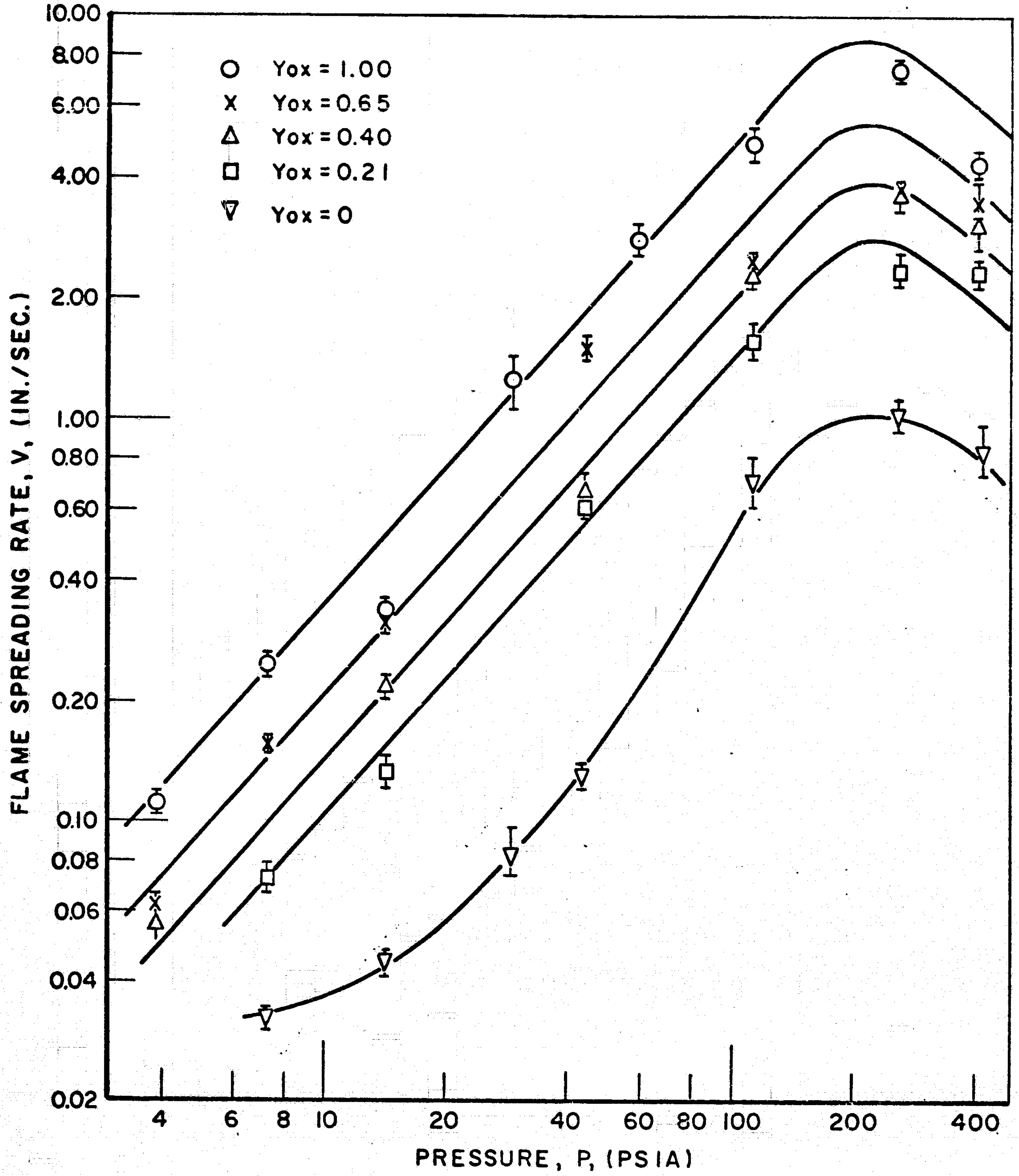


FIG. 2. LOG V VERSUS LOG P FOR ICRPG REFERENCE COMPOSITE PROPELLANT IN O_2/N_2 ENVIRONMENTS

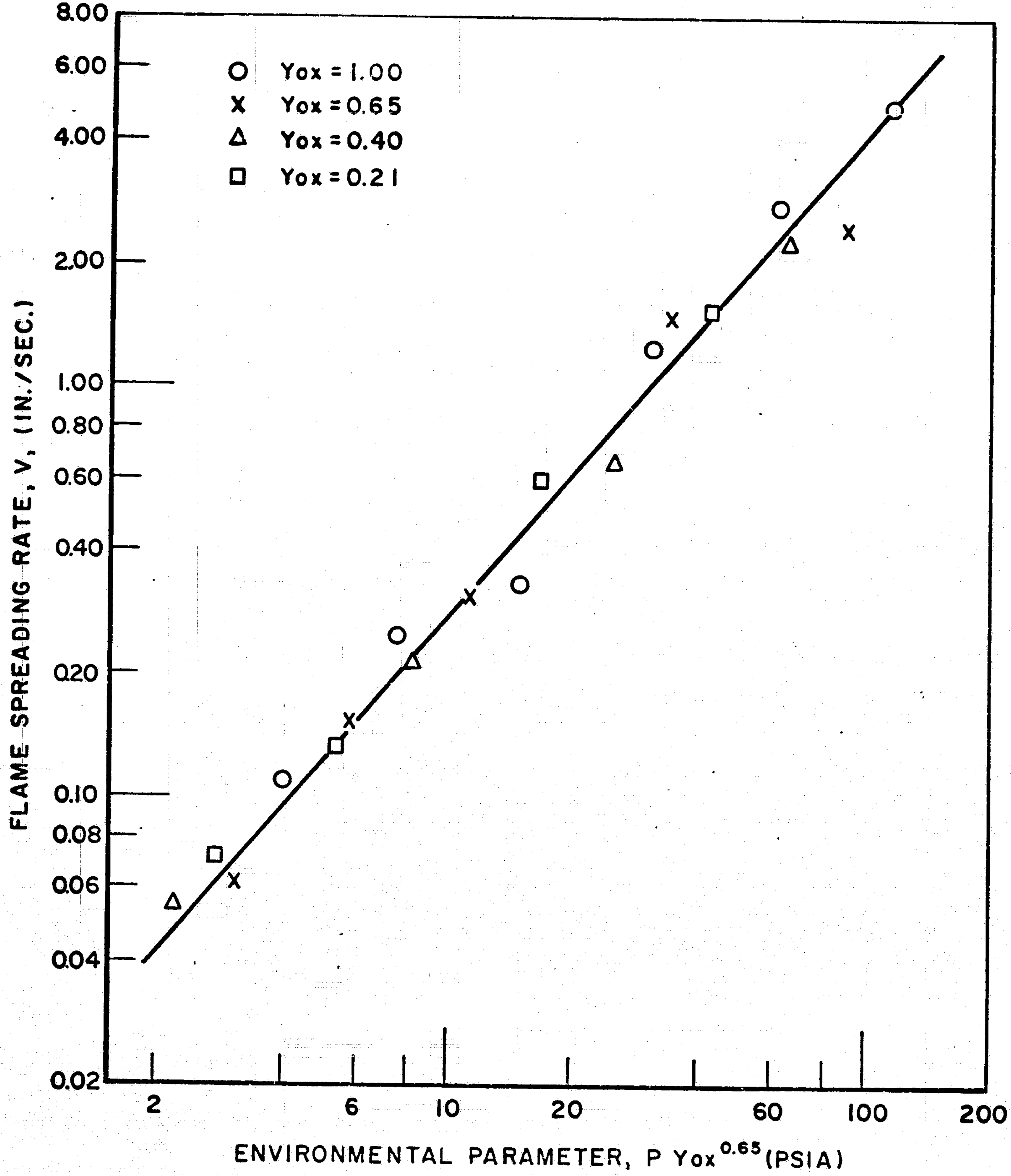


FIG. 3. LOG V VERSUS LOG P $Yox^{0.65}$ FOR ICRPG REFERENCE COMPOSITE PROPELLANT FOR PRESSURES BETWEEN 4 AND 115 PSIA IN O_2/N_2 ENVIRONMENTS

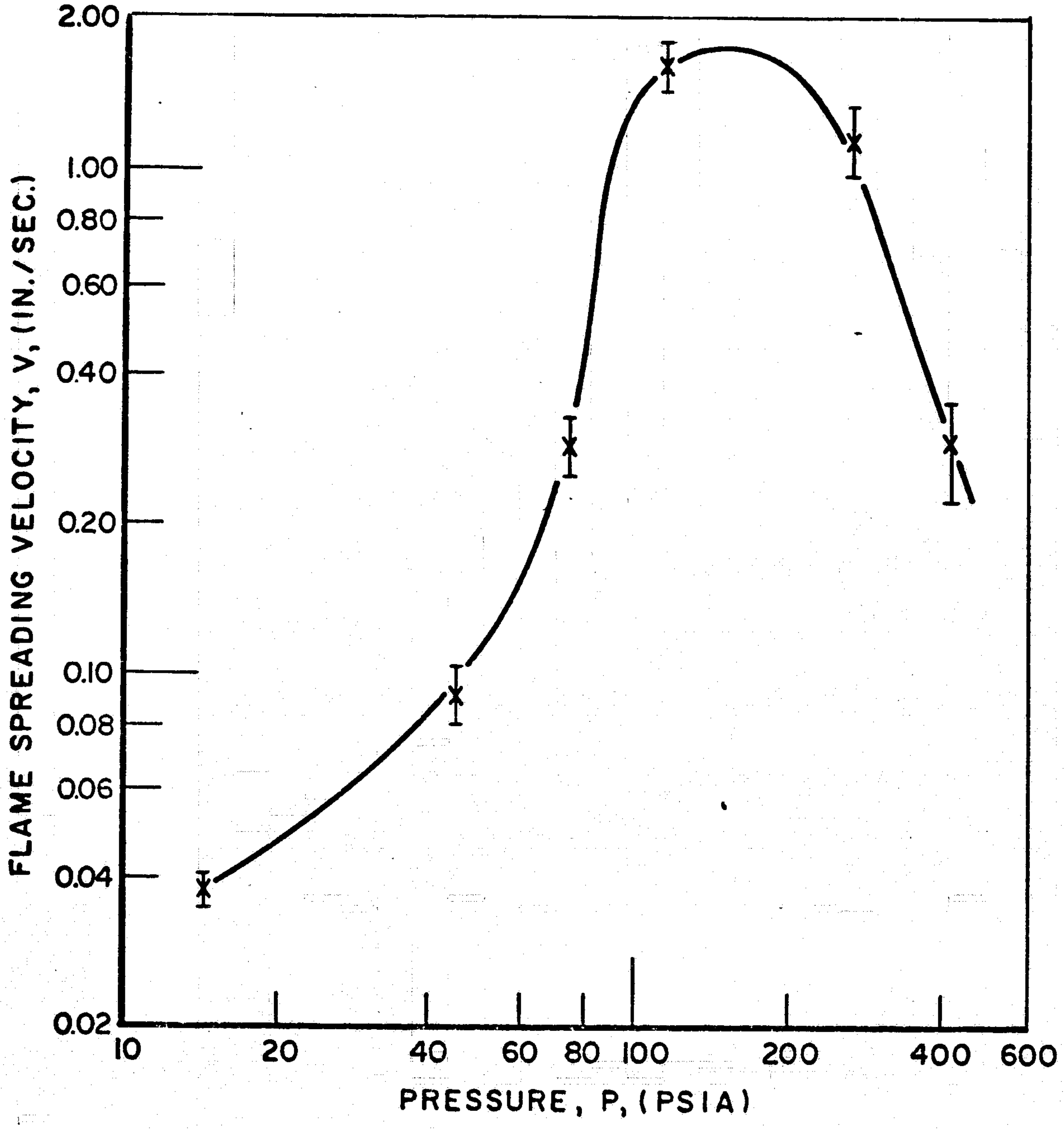


FIG. 4. LOG V VERSUS LOG P FOR ICRPG REFERENCE COMPOSITE PROPELLANT IN METHANE

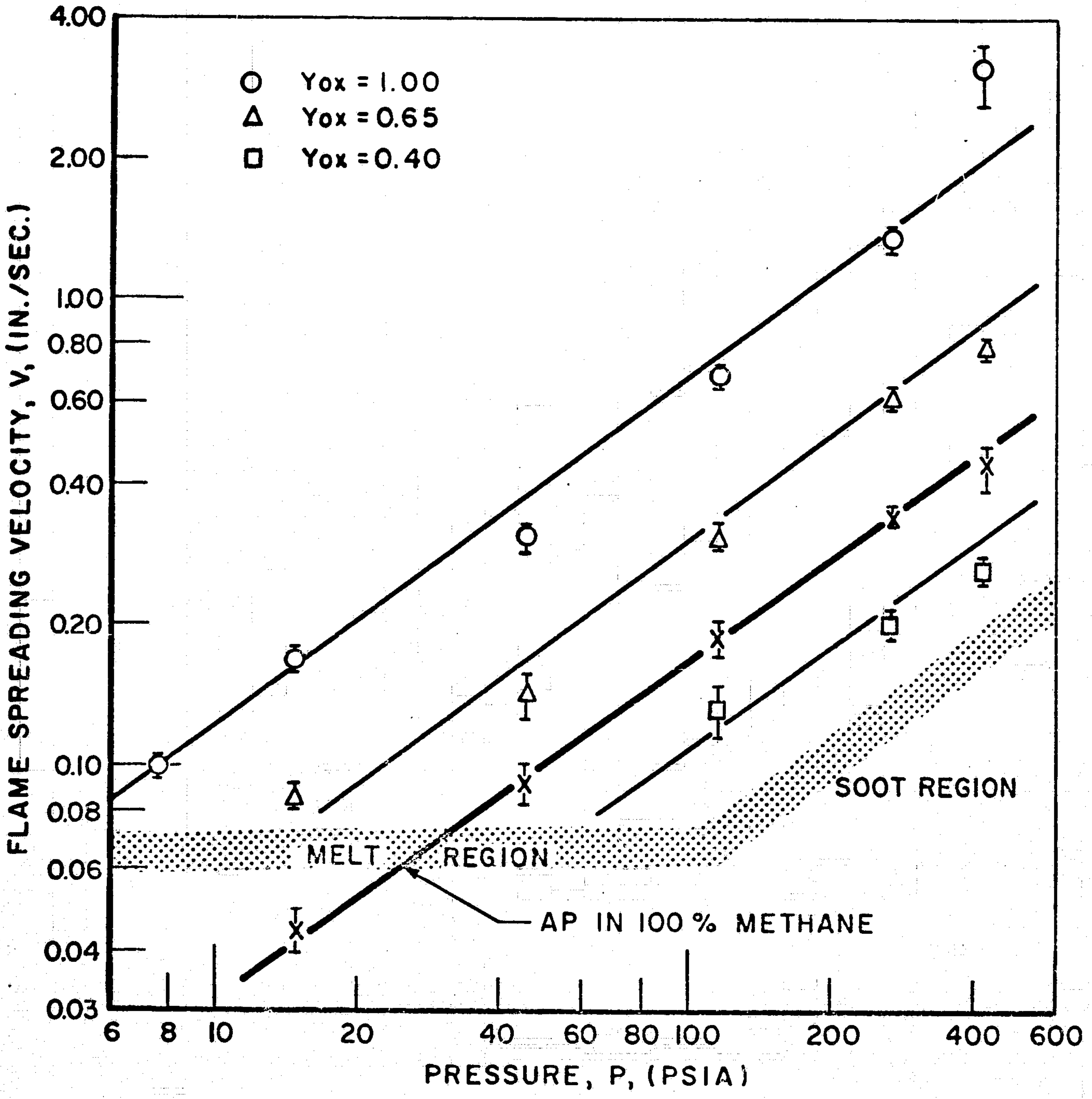


FIG. 5. LOG V VERSUS LOG P FOR ICRPG BINDER IN O_2/N_2 ENVIRONMENTS

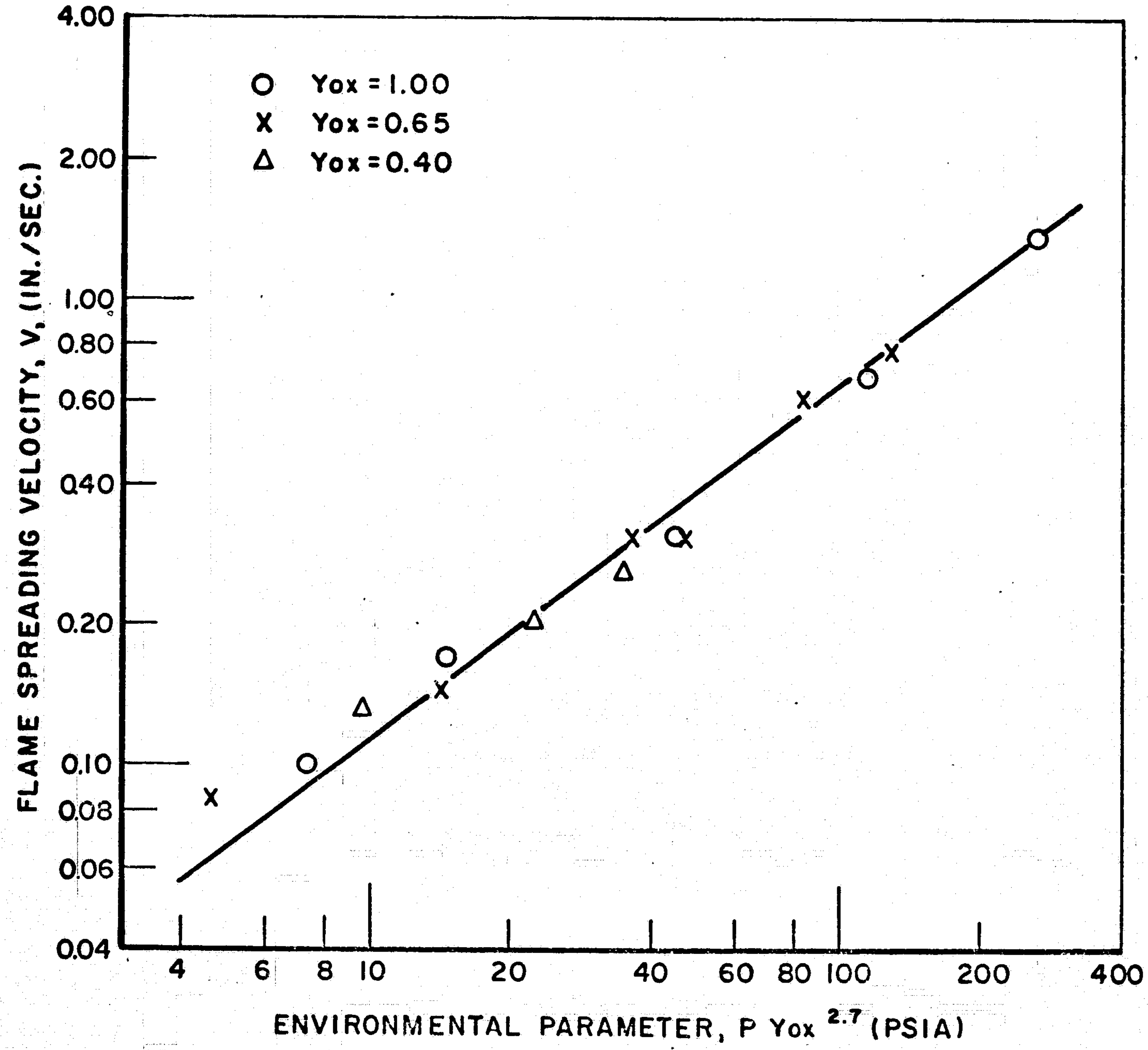


FIG. 6. LOG V VERSUS LOG P$Y_{ox}^{2.7}$ FOR ICRPG BINDER IN O_2/N_2 ENVIRONMENTS

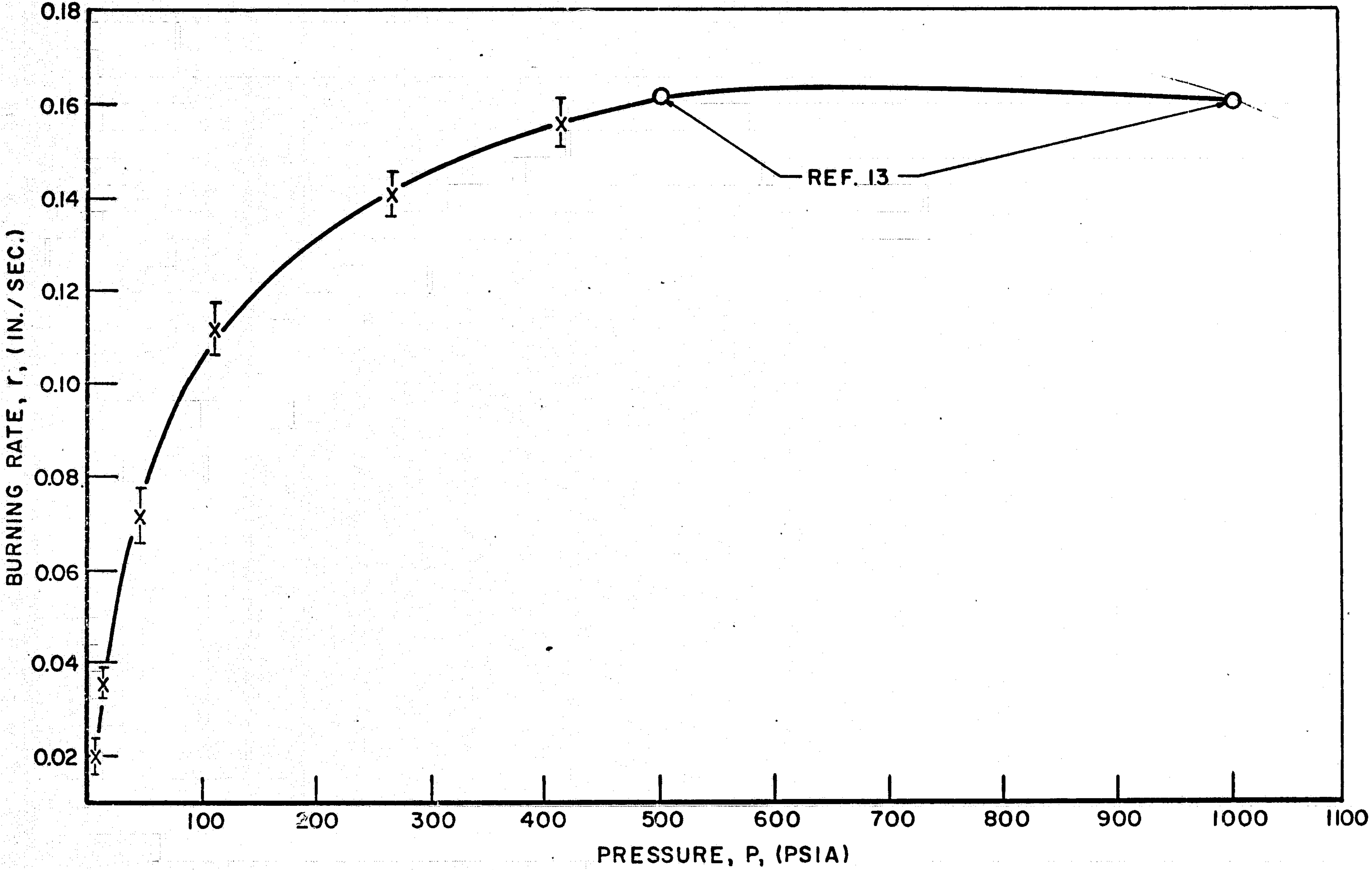


FIG. 7. r VERSUS P FOR ICRPG REFERENCE COMPOSITE PROPELLANT

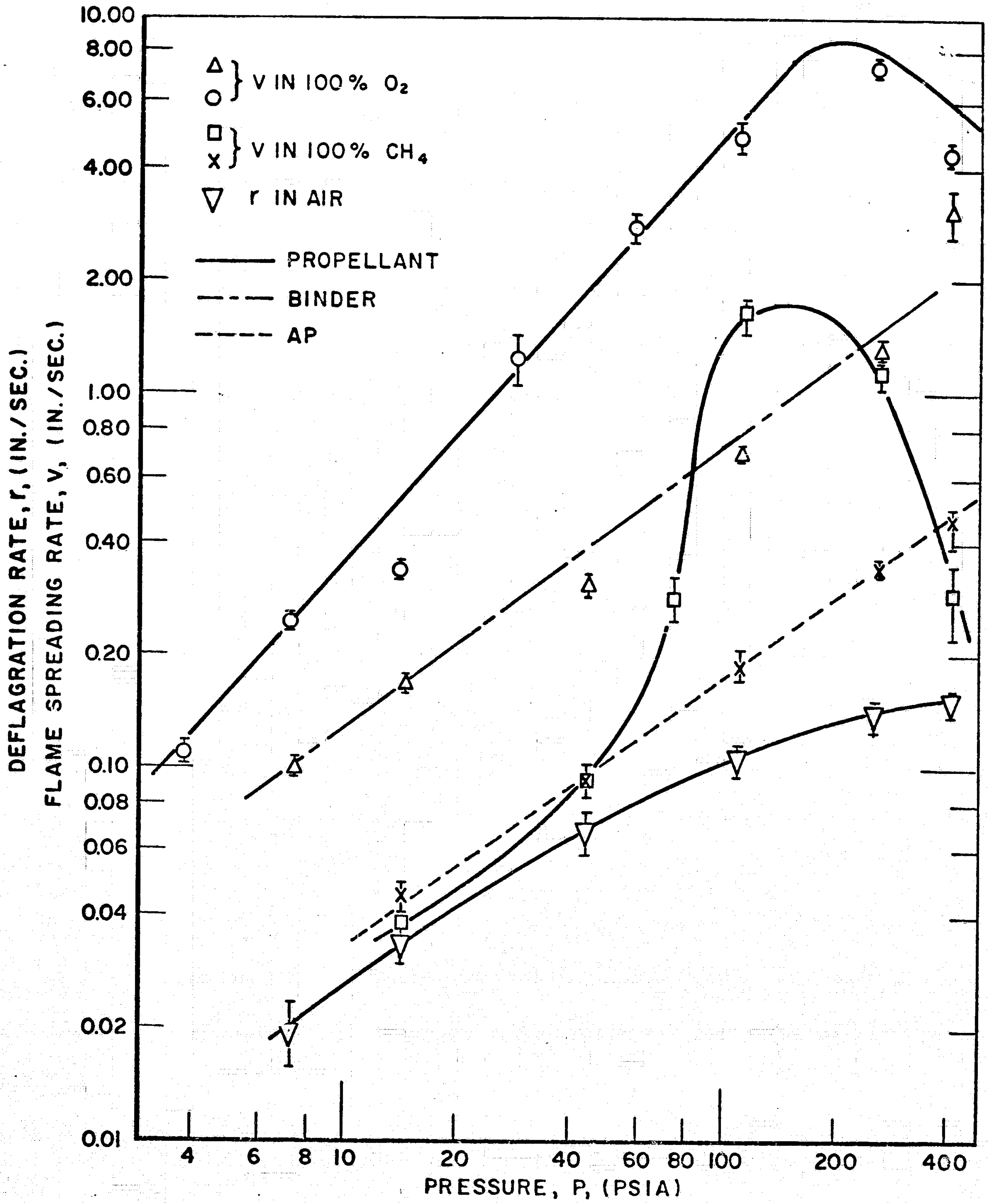


FIG. 8. COMPARISON OF LOG V AND LOG r VERSUS LOG P FOR ICRPG PROPELLANT AND CONSTITUENTS IN VARIOUS ENVIRONMENTS

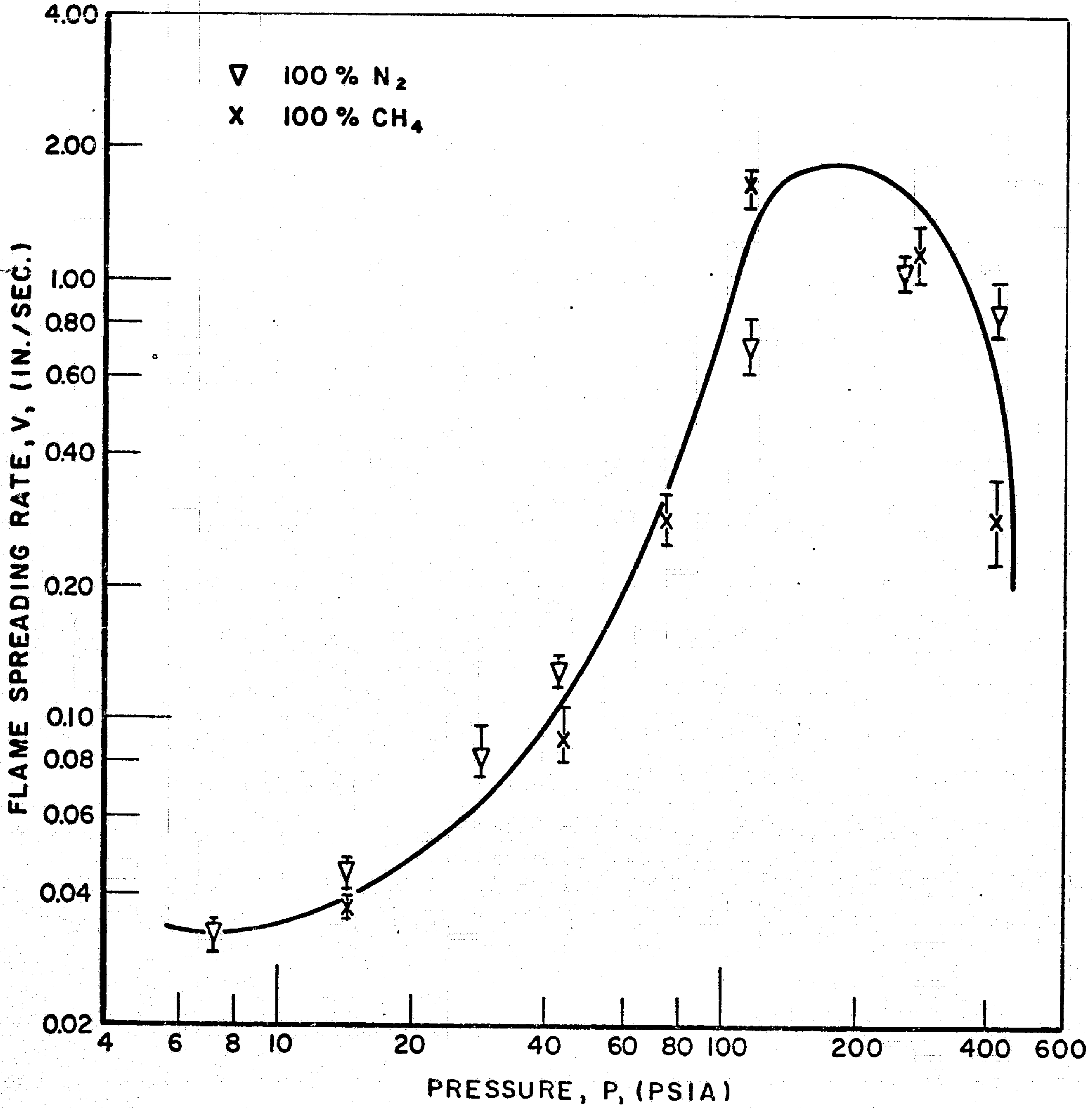


FIG. 9. COMPARISON OF LOG V VERSUS LOG P FOR ICRPG PROPELLANT IN NITROGEN AND METHANE ENVIRONMENTS

PART II

FLAME SPREAD OVER FUEL BEDS: SOLID PHASE ENERGY CONSIDERATIONS

FLAME SPREAD OVER FUEL BEDS: SOLID-PHASE ENERGY CONSIDERATIONS

F. A. LASTRINA, R. S. MAGEE, AND R. F. McALEVY III

Combustion Laboratory, Stevens Institute of Technology, Hoboken, New Jersey

This paper reports on an analytical and experimental investigation of flame spread over the surface of a solid-fuel bed in an oxygen-inert environment. It is postulated that the processes controlling the flame-spreading phenomenon occur in a very small "ignition region" at the leading edge of the spreading flame adjacent to the surface, and attention is focused on this small region. The solid-phase energy equation is uncoupled from the gas-phase conservation equations and solved separately, retaining as a boundary condition the heat flux into the surface from the adjacent gas phase. The resulting solutions in the form of simple algebraic equations, show clearly the different relationships between the physically important parameters associated with flame propagation over: (1) a "thick" fuel bed (thermal wave penetration into the solid beneath the ignition region much less than the fuel-bed depth), and (2) a "thin" fuel bed (subsurface temperature gradients negligible). The "critical thickness" criterion for separating the regions of thin and thick fuel-bed flame-spreading characteristics evolves as a naturally occurring parameter of the problem. The main dependence of heat flux on environmental parameters is obtained from consideration of the gas-phase conservation equations in a quiescent environment. By combining the results from the gas-phase and solid-phase analyses, simple algebraic relationships are obtained between flame-spreading velocity and parameters of theoretical and practical interest. Experimentally, using the techniques described in Ref. 1, the dependence of flame-spreading velocity on pressure level, oxidant mole fraction, diluent gas, initial temperature, and fuel-bed depth is determined for polymeric and cellulosic materials. In addition the influence of forced convective motion of the environment on flame spreading velocity is investigated experimentally. The analytical results provide excellent correlation for all data obtained in a quiescent environment, with the exception of the influence of initial temperature. Data obtained by other investigators are shown to be correlated as well. It is concluded that the role played by the solid phase in the over-all flame-spreading mechanism is generally understood, but the gas-phase processes require further definition.

Background and Introduction

Extensive experiments by McAlevy and Magee[1] in quiescient O_2/inert environments have shown that the flame-spreading velocity (V) over horizontal fuel beds is a strong function of environmental pressure level (P) and oxygen mole fraction (Y_{ox})—and all of their data could be correlated by a power-law relationship of the form $V \propto (PY_{ox}{}^m)^\Phi$. In addition, they found that the fuel-bed surface temperature abruptly increased from its initial value T_0 to the fuel "burning temperature" T_b, in a very small distance δ. (For polymethylmethacrylate, the fuel burning temperature was approximately 750°F independent of the gas-phase environmental conditions, and δ varied from 0.06 in. to 0.15 in., depending on the gas-phase environmental conditions.) Following the steep temperature rise, the surface temperature was found to remain constant at T_b. They postulated that V is controlled by the processes taking place within the small distance δ, the "ignition region" at the leading edge of the spreading flame adjacent to the surface. A continuous, diffusive gas-phase ignition model of the flame-spreading phenomenon was postulated and a simplified analysis of this model, supplemented by experimentally determined surface-temperature profiles in the ignition region, yielded the same power-law relationship as that exhibited experimentally. It was concluded that gas-phase processes in the ignition region strongly influence the flame-spreading phenomenon. The solid phase was not considered explicitly, so its influence on the phenomenon could not be assessed.

Other models of the phenomenon have been presented by de Ris[2] and by Sanchez Tarifa et al.[3]

Unfortunately, in both cases, their analyses result in expressions that are sufficiently complex to preclude the prediction of the influence of P and Y_{ox} on the flame-spreading velocity. Hence, it is impossible to assess the degree to which their models and subsequent analyses are supported by experiments involving variation of these important gas-phase parameters.

de Ris solved the coupled gas and solid phase conservation equations for V by neglecting the existence of the ignition region, and assumed instead that the classical "thin"-flame approximation is applicable down to the solid surface. This allowed the flame-spreading problem to be treated by an extension of the Schavb–Zeldovitch formulation of the laminar diffusion flame problem.

The thin flame approximation is probably valid at distances relatively far from the ignition region since it is reasonable to expect in this region that the ratio of mass transport time to chemical reaction time, i.e. Damkoler number,[6] is large. However, in the ignition region, heat loss to the solid and a paucity of fuel vapors must result in a relatively low reaction intensity. Thus, in the ignition region, the Damkoler Number will be relatively small and hence the thin-flame assumption is probably invalid.

This paper presents the results of a further theoretical investigation of events occurring in the ignition region, both in the solid and gas phases. Analytical expressions are obtained which, when combined with empirical results, successfully "predict" the influence of *both* solid- and gas-phase parameters on the flame-spreading velocity. Also presented are new experimental data which are shown to be generally consistent with these analytical results. Data obtained by other investigators are shown to be consistent as well.

Theory

Analytically, in the ignition region, the solid-phase energy equation and the gas-phase conservation equations are uncoupled from each other, and solved separately. The resulting solutions are then combined by equating the total heat flux from the gas phase to the total heat flux conducted into the fuel-bed interior.

Solid-Phase Energy Equation

In the ignition region, the extent of which is defined by δ, the temperature of a surface element increases from its initial value T_0 to the fuel "burning temperature" T_b, due to heat feedback from chemical reaction in the adjacent gas phase. Downstream of δ, T_b remains constant. The time required to heat the surface from T_0 to T_b, the ignition period, is the time for the flame to propagate the distance δ, i.e. δ/V, where V is the flame-spreading velocity.

Assuming that heat conduction through the solid in the direction of flame propagation is negligible compared to heat conduction normal to the fuel-bed surface, the solution to the one-dimensional, unsteady heat-conduction equation with appropriate boundary conditions results in the temperature profile below each incremental element of surface in the ignition region as a function of time.

Consider a fuel bed of thickness (τ) with the y coordinate attached to an insulated bottom surface. Assuming as a first approximation that the heat flux to the surface is constant in the ignition region $\dot{q}(t) = \dot{q}_1$, the heat-conduction equation and appropriate boundary conditions are

$$\partial T'/\partial t = (K_s/\rho_s C_s)(\partial^2 T'/\partial y^2); \qquad (1)$$

Boundary Conditions:

$$\begin{aligned} t<0:&\quad T'=0, && \text{all } y;\\ t>0:&\quad K_s(dT'/dy)=\dot{q}_1 && y=\tau;\\ &\quad dT'/dy=0 && y=0, \end{aligned}$$

where $T' = (T(y,t) - T_0)$; K_s, ρ_s, and C_s are the thermal conductivity, the density, and the specific heat of the solid, respectively.

The solution to Eq. (1) is found in Ref. 9, [p. 112, Eq. (4)], and is given by

$$T' = (2\dot{q}_1/K_s)[K_s t/\rho_s C_s]^{1/2} \times \sum_{N=0}^{\infty}\left[i\,\text{erfc}\,\frac{(2N+1)\tau - y}{2(K_s t/\rho_s C_s)^{1/2}} + i\,\text{erfc}\,\frac{(2N+1)\tau + y}{2(K_s t/\rho_s C_s)^{1/2}}\right]. \qquad (2)$$

Using the fact that, along the flame-spreading surface ($y = \tau$), the surface temperature equals the fuel burning temperature at time δ/V, Eq. (2) becomes

$$T_b - T_0 = \dot{q}_1\delta(K_s\rho_s C_s\delta V)^{-1/2}[2i\,\text{erfc}\,0 + 2 \sum_{N=0}^{\infty} 2i\,\text{erfc}\,(N+1)\bar{\tau}], \qquad (3)$$

where

$$\bar{\tau} = \tau/(K_s\delta/\rho_s C_s V)^{1/2} \qquad (4)$$

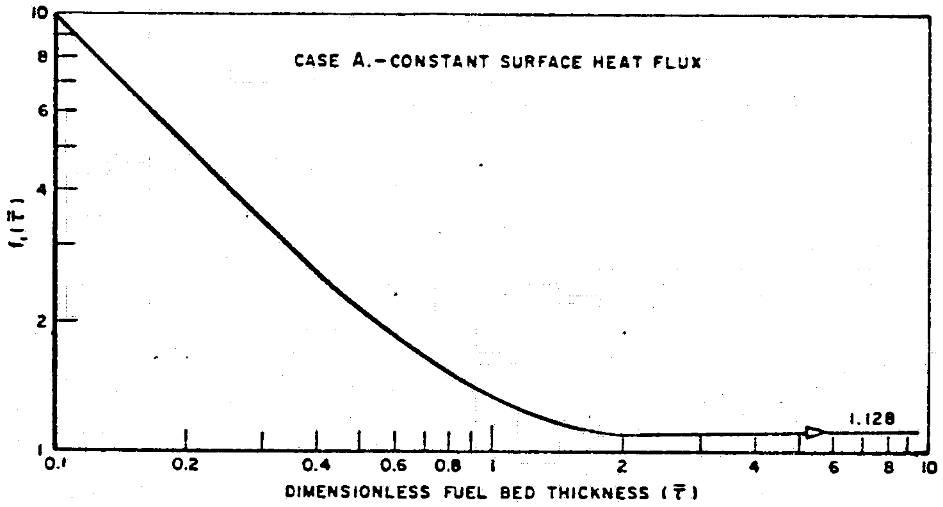


FIG. 1. $f_1(\tau)$ vs τ.

is the dimensionless fuel-bed thickness, i.e., the ratio of fuel-bed thickness to thermal-wave penetration depth. But $\bar{q}_1\delta$ is nothing more than the total heat flux into the solid-fuel bed (i.e., the heat flux to the surface minus the heat flux absorbed by the fuel-vaporization process), $\dot{Q}_s$, so Eq. (3) becomes

$$T_b - T_0 = \dot{Q}_s(K_s\rho_s C_s\delta V)^{-1/2}f_1(\bar{\tau}), \qquad (5)$$

where $f_1(\bar{\tau})$ is defined as

$$1.128 + 2\sum_{N=0}^{\infty} 2i \operatorname{erfc}(N+1)\bar{\tau}.$$

From Fig. 1, a log–log plot of $f_1(\bar{\tau})$ versus $\bar{\tau}$, it is apparent that for $\bar{\tau} > 1.0$, $f_1(\bar{\tau})$ equals 1.128; and for $\bar{\tau} < 1.0$, $f_1(\bar{\tau})$ equals $1/\bar{\tau}$. Therefore, Eq. (5) can be rewritten as

$$\dot{Q}_s = 0.89(K_s\rho_s C_s V)^{1/2}(T_b - T_0)$$
$$\bar{\tau} > 1.0 \text{ (thick fuel bed)}, \qquad (6)$$

and

$$\dot{Q}_s = \rho_s C_s V'\tau'(T_b - T_0)$$
$$\bar{\tau} < 1.0 \text{ (thin fuel bed)}, \qquad (7)$$

where V' is the thin fuel-bed flame-spreading velocity (as opposed to the symbol V used for the thick fuel bed flame spreading velocity) and τ' is the thin fuel-bed thickness. Hence, a natural criterion, $\bar{\tau} \simeq 1.0$, evolves from the analysis, which defines the critical thickness separating thin from thick fuel-bed behavior.

[Note: Analytical solutions, which differ only by a numerical coefficient from those shown in Eqs. (6) and (7), have been obtained by (i) a control volume approach which employed, as boundary conditions, assumed surface-temperature distributions, and (ii) an approach identical to that reported above, but assuming a linearly increasing surface heat flux.[4]]

Gas-Phase Conservation Equations

For present purposes, the gas-phase ignition region of extent δ is viewed as one dominated by diffusion and chemical reaction, but not by convection. Consequently, convective effects are neglected in the following analysis.

Local chemical reaction rate depends on local reactant concentration and local temperature. As the fuel-vapor concentration C_f decreases and the gas temperature T_g increases with distance from the fuel surface, the local reaction rate reaches a maximum at some distance above the surface. This in turn results in a local maximum temperature at a location $\tilde{y}(x)$. It will be assumed that $\tilde{y}(x)$ is very small compared to δ, so that gradients in the x direction are neglected compared to gradients in the y direction. Thus, the rate of heat conduction to the solid surface is assumed large compared to the rate of heat conduction forward through the gas phase and, consequently, the latter is neglected.

Assuming that second-order Arrhenius kinetics describe the chemical heat-release process in the gas phase, and that density (ρ), thermal conductivity (K), specific heat (c), and oxygen concentration (C_{ox}) are constant throughout the ignition region, the energy and fuel conservation equations become:

$$\alpha(\partial^2 T_g/\partial y^2) = -(Q_c/\rho c)C_f C_{\text{ox}} A \exp(-E/RT_g) \qquad (8)$$

and

$$D(\partial^2 C_f/\partial y^2) = C_f C_{\text{ox}} A \exp(-E/RT_g) \qquad (9)$$

where: Q_c is the heat released per unit of fuel burned, α the thermal diffusivity, D the mass diffusivity, and E and A the activation energy and pre-exponential factor, respectively, of the Arrhenius function. Defining the following dimensionless parameters,

$$\theta = (T_g - T_v)/(Q_c/c), \qquad \xi = C_f/C_{f,\delta},$$
$$Y_{\text{ox}} = C_{\text{ox}}/\rho, \quad \text{and} \quad \eta = y/(\alpha/c_{f,\delta}A)^{1/2},$$

where $C_{f,\delta}$ is the maximum concentration of fuel vapor in the ignition region, that is, at the fuel surface at $X = \delta$, the conservation equations become

$$(\partial^2\theta/\partial\eta^2) = -Y_{\text{ox}}\xi \times \exp -\{(E/R)(T_b + \theta Q_c/c)^{-1}\} \qquad (10)$$

$$\partial^2\xi/\partial\eta^2 = Y_{\text{ox}}(\alpha/D)(\rho/C_{f,\delta})\xi \times \exp -\{(E/R)(T_b + \theta Q_c/c)^{-1}\}. \qquad (11)$$

Integration of the energy equation between the surface $y = \eta = 0$ and the plane of maximum temperature $y = \tilde{y}(x)$ [or $\eta = \tilde{\eta}(x)$] yields

$$\left.\frac{\partial\theta(x)}{\partial\eta}\right|_0 = Y_{\text{ox}} \int_0^{\eta(x)} \xi \times \exp -\{(E/R)(T_b + \theta Q_c/c)^{-1}\}\, d\eta, \qquad (12)$$

which when integrated along the surface from $x = 0$ to $x = \delta$, yields:

$$\int_0^\delta \left.\frac{\partial\theta(x)}{\partial\eta}\right|_0 dx = Y_{\text{ox}} \int_0^\delta \left[\int_0^{\eta(x)} \xi \times \exp -\{(E/R)(T_b + \theta Q_c/c)^{1/2}\}\, d\eta\right] dx. \qquad (13)$$

The naturally occurring length scale of the problem is assumed to be the same in the x and y direction, namely $(\alpha/C_{f,\delta}A)^{1/2}$.
Thus, defining

$$\bar{\delta} = \delta/(\alpha/C_{f,\delta}A)^{1/2} \quad \text{and} \quad \bar{x} = x/(\alpha/C_{f,\delta}A)^{1/2},$$

Eq. (13) becomes

$$\int_0^{\bar\delta} \left.\frac{\partial\theta(\bar{x})}{\partial\eta}\right|_0 d\bar{x} = Y_{\text{ox}} \int_0^{\bar\delta} \left[\int_0^{\eta(\bar{x})} \xi \times \exp -\{(E/R)(T_b + \theta Q_c/c)^{-1}\}\, d\eta\right] d\bar{x} \qquad (14)$$

or

$$\int_0^{\bar\delta} \left.\frac{\partial\theta(\bar{x})}{\partial\eta}\right|_0 d\bar{x} = Y_{\text{ox}} F(P, Y_{\text{ox}}), \qquad (15)$$

where $F(P, Y_{\text{ox}})$ represents the integral, which is an implicit function of P and Y_{ox} through $\xi(P, Y_{\text{ox}})$.

Finally, the total heat flux to the fuel surface in the ignition region can be written as:

$$\dot{Q}_s = k(Q_c/c) Y_{\text{ox}} F(P, Y_{\text{ox}}). \qquad (16)$$

Combination of Results from the Gas-Phase Analysis with the Results from the Solid-Phase Analysis

Assuming that the energy conducted into the surface from the gas phase is equal to the energy conducted away from the surface into the fuel bed, that is, the energy absorbed by surface vaporization is negligible, the right-hand side of Eq. (16) can be combined with the algebraic relationships derived from the solid-phase energy equation to yield

Thin Fuel Bed:

$$V' \simeq \frac{kQ_c Y_{\text{ox}} F(P, Y_{\text{ox}})}{\rho_s c_s c\tau'(T_b - T_0)}; \qquad (17)$$

Thick Fuel Bed:

$$V \simeq \frac{\{kQ_c Y_{\text{ox}}^2 [F(P, Y_{\text{ox}})]\}^2}{\rho_s c_s c^2 K_s \delta (T_b - T_0)^2}. \qquad (18)$$

Experiments—Results—Conclusions

This section is organized in segments. In the first, results obtained from a numerical integration of the solid-phase energy equation are discussed, and in the remaining segments, successively, some experiments by the authors as well as other investigators, the results from these experiments and their comparison with the subject analytical work are presented.

Comparison with Numerical Solution

Values of $\dot{Q}_s$ were calculated using Eq. (6) by employing empirical values of $V(P, Y_{ox})$ and $\delta(P, Y_{ox})$ for a variety of environmental conditions. Values of $\dot{Q}_s$ were also obtained by numerical integration of the *two-dimensional* solid-phase energy equation in the ignition region, employing as boundary conditions the empirically determined surface-temperature distributions of Ref. 1. These values, obtained by the two methods, are in excellent agreement, justifying the underlying assumptions employed in the solid-phase analysis, e.g., neglection of heat transport through the solid phase in the direction of flame propagation, and therefore demonstrating the applicability of Eq. (6) to the flame-spreading problem.[4]

Flame-Spreading Characteristics of Thin and Thick Cellulosic Specimens

The flame-spreading velocity over the surface of cellulosic specimens was measured in quiescent environments of various pressures and compositions. The apparatus and experimental procedure employed are described in Ref. 1. Test specimens were fabricated from 3 × 5 in., white unruled index cards, 0.0088 in. thick. Specimens of varying thickness were made by a lamination technique. Individual cards were soaked in water, superposed on each other, and pressed together at a nominal pressure of 15,000 psi. The specimens were allowed to room-dry overnight and then dried for at least one hour in an oven at 220°F. Single cards were also dried to remove any moisture they might have absorbed. The speci-

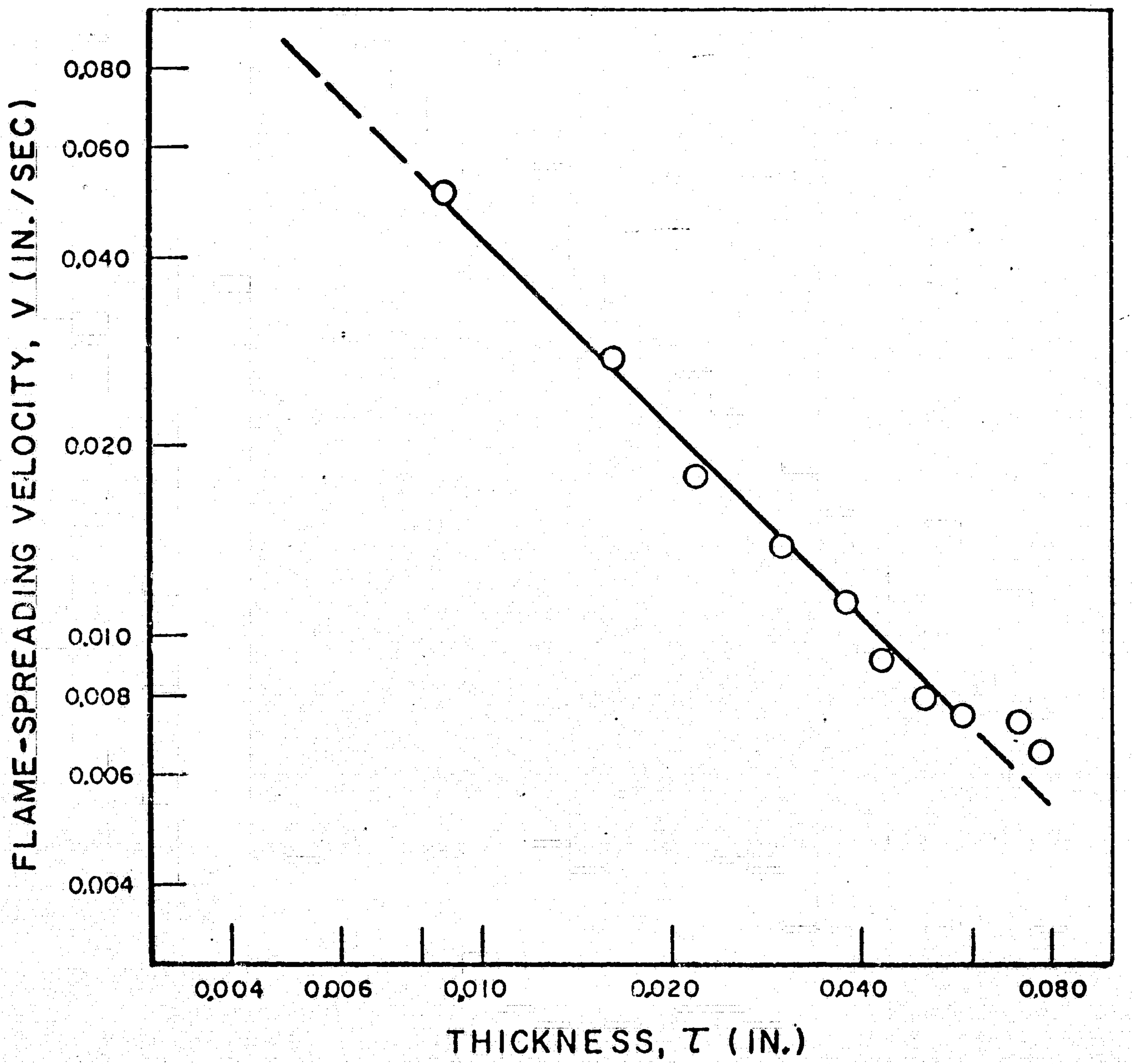


FIG. 2. V vs τ for cellulosic specimens in air at 1 atm.

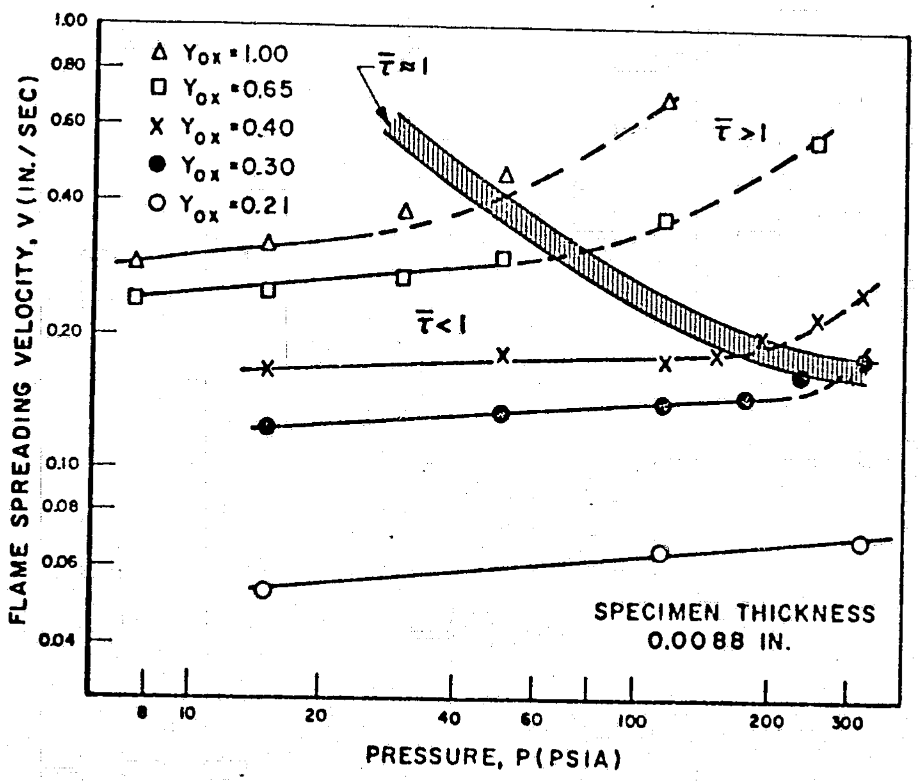


FIG. 3. V vs P for "thin" cellulosic specimens in O_2/N_2 environments.

mens were mounted vertically in an asbestos holder which inhibited the edge-effect noted previously.[1,7] The specimens were then ignited at the top and the flame spread evenly down both sides.

Figure 2 shows the effect of varying thickness on the flame-spreading velocity in air at 1 atm. Over a substantial range of the thicknesses tested (0.0088 to 0.077 in.), the flame-spreading velocity varies inversely with the specimen thickness. For specimens thicker than 0.060 in., or so, there is an indication that V is less sensitive to thickness. Unfortunately, it was not possible to obtain data for thicker samples at these environmental conditions, as the flame appeared to become unstable and quenched after ignition.

Further tests were performed with single-card specimens and the results plotted in Fig. 3. Equation (4) was employed to calculate the shaded area ($\bar{\tau} \simeq 1$) between the regime of thin fuel-bed flame-spreading characteristics ($\bar{\tau} < 1$) and thick fuel-bed characteristics ($\bar{\tau} > 1$). The data support the validity of this criterion. In the region of thin fuel-bed characteristics, $V'(P, Y_{ox})$ is well represented by means of a power law. The pressure exponent is small (ranging between 0.05 and 0.1)—but not zero as predicted by de Ris[2]—while the dependence on Y_{ox} is much stronger ($V' \sim Y_{ox}^{0.9}$).

In the region of thick fuel-bed characteristics, experiments with laminated specimens ($\tau = 0.077$ in.) indicated that $V(P, Y_{ox}) \sim Y_{ox}^{2.1}P^{.63}$. These data are represented in Fig. 4. The data of Figs. 3 and Figs. 4 can be used to obtain information concerning $F(P, Y_{ox})$. This function appears in both Eqs. (17) and (18). Since Eq. (17) predicts $V' \propto Y_{ox}F(P, Y_{ox})$, and the data in Fig. 3 can be correlated by $V' \propto Y_{ox}^{0.9}P^{0.05}$, $F(P, Y_{ox})$ is a very weak function of P and Y_{ox}. From previous measurements on thick fuel beds it was found that $\delta \sim P^{-0.5}$ (Ref. 1). Thus, Eq. (18) can be written as $V \propto Y_{ox}^2P^{0.5}F(P, Y_{ox})$. Comparison with the empirical power law $V \propto Y_{ox}^{2.1}P^{0.63}$ indicates again that $F(P, Y_{ox})$ is a very weak function of P and Y_{ox}. For other materials and environmental conditions this dependence might change somewhat. Unfortunately, data for *both* thin and thick specimens of materials other than cellulose are nonexistent. However, data obtained previously for thick PPM specimens in O_2/N_2 environments, indicated $V \propto Y_{ox}^{2.46}P^{0.82}$ (Ref. 1). This suggests that $F(P, Y_{ox}) \propto Y_{ox}^{0.23}P^{0.16}$ for PMM, a dependence slightly different than that for cellulose. It is believed, in the case of cellulose, that a combination of data scatter and curve-fitting errors accounts for the discrepancy of the Y_{ox} dependence of $F(P, Y_{ox})$. (In the case of the thin fuel bed, the exponent $\simeq -0.1$, while for thick beds, the exponent $\simeq 0.1$.)

The ability to successfully correlate the observed flame-spreading characteristics of both

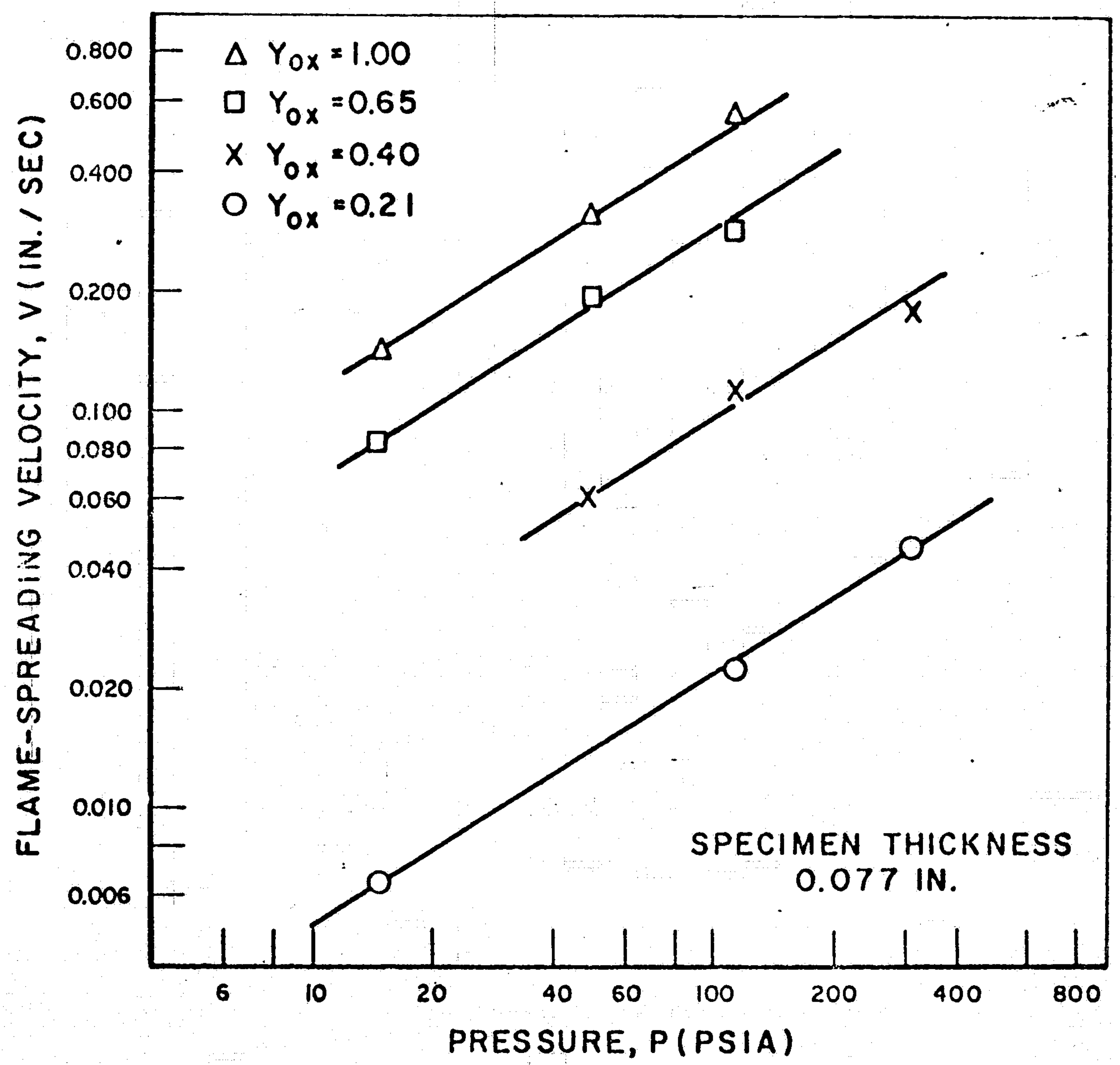


FIG. 4. V vs P for "thick" cellulosic specimens in O_2/N_2 environments.

the thin and thick cellulosic fuel beds, tends to verify the validity of flame-spreading equations (17) and (18).

Flame Spreading Over Various Materials—Thin and Thick Fuel Specimens

The influence of oxygen concentration on flame propagation over a variety of fuel materials in quiescent environments was obtained experimentally by Huggett et al.[10] These authors attempted to correlate the flame-spreading velocity with the logarithm of the specific heat of the gas mixture divided by the oxygen mole fraction, i.e. $V \propto \log(c/Y_{ox})$. Figure 5, which shows typical data obtained by Huggett et al., demonstrates that the flame-spreading data can also be correlated equally well by $V \propto (C/Y_{ox})^{-b}$.

According to Eqs. (17) and (18), and the results reported for cellulose which implied that $F(P, Y_{ox})$ is a weak function of P and Y_{ox}, V should be proportional to $(c/Y_{ox})^{-b}$, where $b \simeq 1.0$ for thin fuel specimens and $b \simeq 2.0$ for thick fuel specimens. Table I lists the type and thickness of the fuel specimen, the empirical exponent b, and the theoretically predicted exponent b. These results, which were not interpreted in this fashion by Huggett et al., are generally consistent with the predicted dependencies of thin and thick fuel beds on oxygen concentration and specific heat of the gas mixture.

Effect of Preheating the Unburned Fuel Bed by a Radiation Source

The influence on flame propagation of preheating the unburned fuel bed was investigated

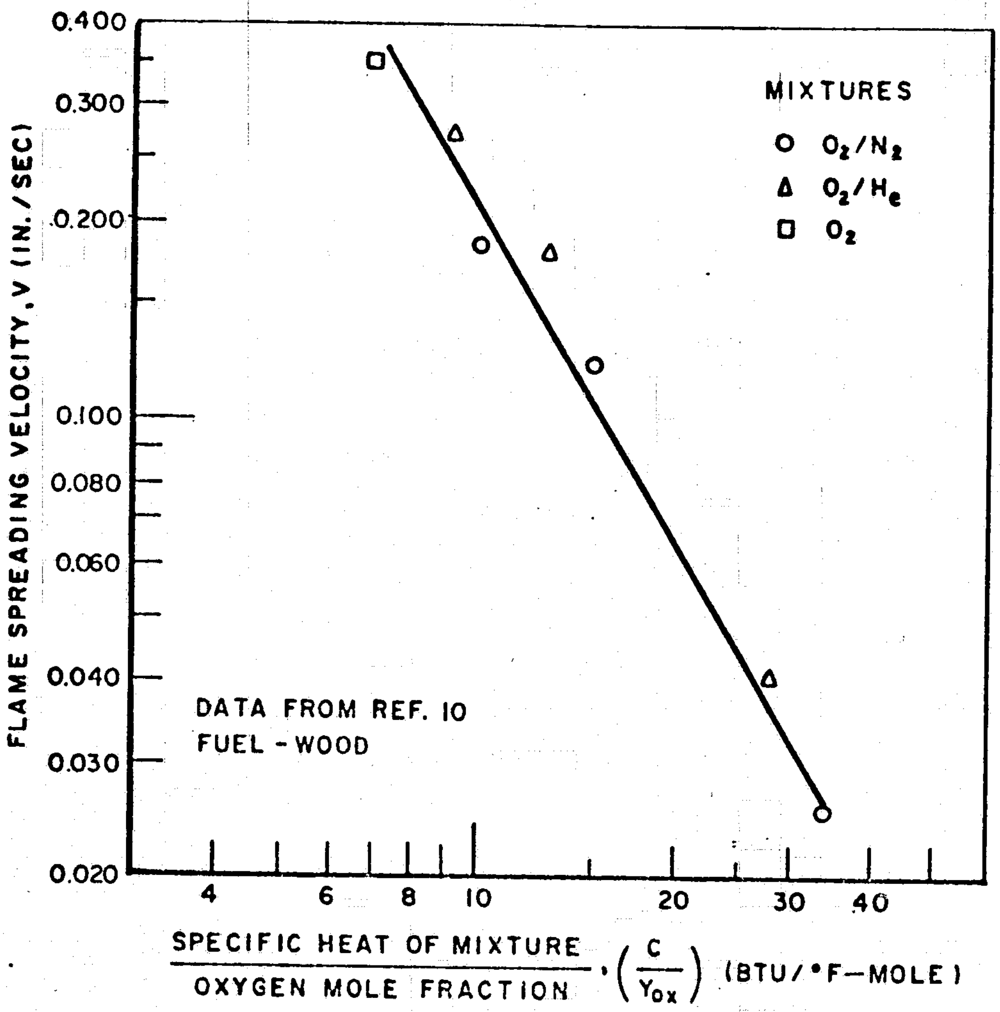


FIG. 5. V vs (c/Y_{ox}) for various O_2/inert mixtures.

by Kwentus in both quiescent and convective flow environments.[11] The fuel bed (12 in. wide by 4 ft. long) consisted of a layer of tamped shredded newsprint (approximately 0.02 in. thick) placed on top of an insulating Fiberglass base. The flame velocity was obtained for various total radiant heat fluxes striking the unburned fuel bed and for various environmental conditions. Typical data of flame velocity (V) versus total radiant heat flux ($\dot{Q}_r$) are shown in Fig. 6. Values of the slopes of V versus $\dot{Q}_r$ varied from 11 in.^{2}/Btu to 20 in.^{2}/Bru, depending on environmental conditions.

For this experiment, the total heat flux to the

TABLE I

Comparison of experimental and predicted exponent of Y_{ox} for thin and thick fuel beds

Fuel specimen			
Material	Thickness (in.)	Empirical exponent*	Predicted exponent†
Paper	0.008	0.96	1.0
Painted surface	0.016	0.91	1.0
Foam cushion	0.250	2.06	2.0
Wood	0.066	1.74	transition thickness
Cellulose acetate	0.250	1.27	2.0

* Data from Ref. 10.

† $b \simeq 1$ for thin fuel specimens; $b \simeq 2$ for thick fuel specimens.

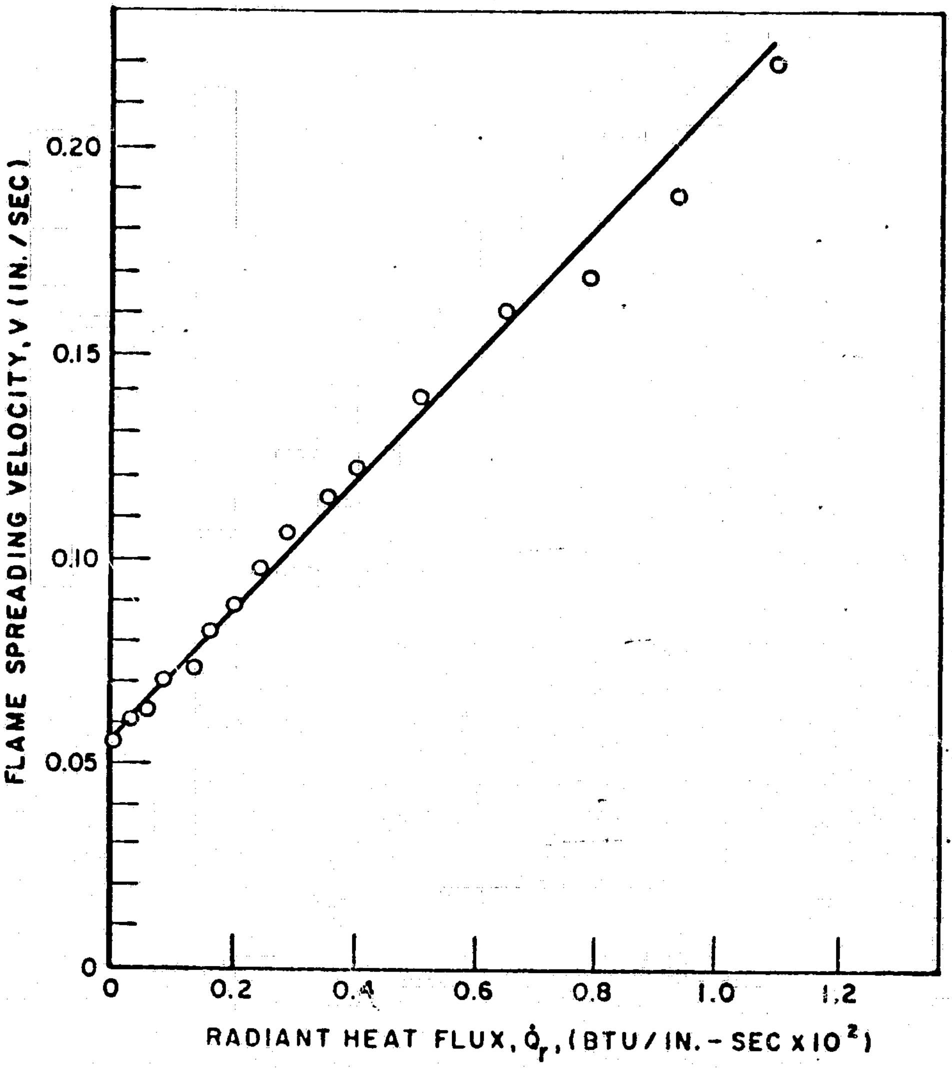


FIG. 6. V vs $\dot{Q}_r$ for shredded newsprint thin fuel bed. (Data from Ref. 11, p. 98, Figs. 4 and 9.)

unburned fuel surface is made up of a normal heat flux from the flame ($\dot{Q}_s$) plus the heat flux from the controlled radiation source ($\dot{Q}_r$). Extending the thin fuel-bed analysis presented herein* [Eq. (7)] for the case of two independent heat fluxes to the surface, it is apparent that

$$\rho_s c_s V \tau' (T_b - T_0) = \dot{Q}_r + \dot{Q}_s,$$

or

$$dV/d\dot{Q}_r = [\rho_s c_s \tau' (T_b - T_0)]^{-1}.$$

The above analysis predicts that the flame velocity should increase linearly with the radiant heat flux; and the slope of this line should equal $1/\rho_s c_S \tau' (T_b - T_0)$. Using appropriate values for $\rho_s \tau'$, c, and $(T_b - T_0)$, the value of the slope is approximately 11 in.^{2}/Btu.[4] Thus, the subject data support the analytical results.

Influence of Initial Temperature on Flame-Spreading Velocity

The influence of the initial temperature of the solid on flame-spreading velocity in a quiescent environment was investigated for both PMM and cellulosic specimens. However, a different experimental procedure was employed for each material.

In the case of PMM, 0.125-in.-thick samples of the solid (0.375 × 3 in.) were mounted horizontally in a test chamber.[1] The chamber was charged with oxygen at atmospheric pressure and the temperature of the top surface, i.e., the flame-spreading surface, was raised to the desired value (up to 223°F) by conductive heating from a strip-heater fastened to the specimen bottom surface. Thermal gradients normal to

---

* The validity of assuming a thin fuel bed cannot be verified since the magnitude of δ, required to determine the critical thickness separating thin from thick fuel beds, is not reported by Kwentus. The thickness of the fuel (0.02 in.) is less than the critical thickness of cellulosic specimens 0.03 in.

TABLE II

Experimental values of n

Fuel	Thin	Thick
PPM	—	1.95
Cellulose	2.5	2.4

the surface were minimized by employing relatively long heating times, e.g., 15 min. The sample was then ignited by an electrically heated wire.

The cellulosic specimens were mounted vertically in an asbestos holder, placed in an isothermal oven (18 × 18 × 15 in.) and heated to the desired temperature (up to 378°F). Once the specimen achieved thermal equilibrium with the surroundings, it was ignited at the top and the flame spread down both sides. Hence, both specimen and environment were at elevated temperature. Both thin (0.0088 in.) and thick (0.077 in.) cellulosic specimens, identical to those referred to earlier, were tested.

The data obtained from these experiments were correlated using the relationship

$$V \propto (T_b - T_0)^{-n},$$

as suggested by Eqs. (17) and (18), to obtain empirical values of n. This required knowledge of T_b for both materials. Values of T_b have been obtained for PMM (750°F),[1] and cellulose (700°F for thin specimens and 780°F for thick specimens.[12] Using these numbers, values for n were extracted and are reported in Table II.

The PPM result is in excellent agreement with the theoretical prediction of Eq. (18), i.e., $n = 2$ for thick fuel beds. While the thick cellulosic specimen results, $n = 2.4$, compares somewhat less favorably with the prediction, the thin-bed cellulosic results, $n = 2.5$, does not support the prediction of $n = 1$. In fact, the temperature sensitivity is approximately the same for both thin and thick cellulosic specimens. Deviation from prediction for cellulosic specimens might be a result of their decomposition process, for, while PMM may be thought to undergo a simple surface decomposition–vaporization process upon application of surface heating, there is evidence that cellulosic materials undergo decomposition in depth.[13]

Thus, the PMM data, and to a lesser extent the thick cellulosic data, support the subject analysis, as well as that of de Ris. But more information concerning the transient thermal decomposition characteristics of cellulosic materials is required before the thin specimen data can be rationalized.

Flame Spreading in Convective Flow Environments Opposed to the Flame Spread

The present support for the proposed flame-spreading mechanism in a quiescent environment suggests that an attempt to analyze flame spread in a convective environment might reasonably be mounted. Its mathematical description is exceedingly more complex (see discussion in Ref. 1) and the solution will require a massive effort. Presented below are some experimental observations that might suggest simplifications to aid the theoretician as well as provide a basis for testing the validity of theoretical predictions.

Experiments were performed in a "blow-down" wind tunnel, driven by high-pressure, bottled test gas. The test-section geometry was 1 × 1 × 12 in. The test gas (O_2/inert mixtures) was admitted through five manifold-holes located in the head end, and swept over 0.125-in.-thick, flush-mounted, test specimens (0.375 in. wide × 4 in. long), located along the centerline with the leading edge 4 in. from the head end of the test section. An inorganic cement was used along the specimen sides to insure that the propagating flame remained planar. The back end of the tunnel was open to the atmosphere.

No attempt was made to measure the velocity profile over the specimen. Instead, the mean flow velocity was calculated from measured mass-flow rates by means of the continuity equation.

Specimens were ignited by an electrically heated wire (certain conditions required the use of an easily ignited ignition charge) at the back end. Flame-spreading-velocity data was only taken over the middle 2 in. Polymethylmethacrylate (PMM) and polyurethane (ICRP) were subjected to test. Typical data are shown in Fig. 7.

All data exhibited increasing flame-propagation velocity with increasing flow velocity until a "critical" flow velocity was reached. All of the data obtained below the critical flow velocity could be correlated by the empirical power-law relationship

$$V \propto U^{0.34} Y_{ox}^{b}, \qquad (20)$$

where U is the test-gas-flow velocity. (This finding contrasts with the de Ris prediction of $V \propto U$.) Values of "b" for both the quiescent and forced convective environments are listed in Table III. The empirical dependence of V on Y_{ox}

TABLE III

Experimental values of b

	PMM		Polyurethane	
	Quiescent b*	Convective b	Quiescent b†	Convective b
O_2/N_2	2.46	1.94	1.95	2.07
O_2/Ar	2.03	2.04	—	2.17
O_2/He	1.48	1.36	—	1.52

* Reference 1.
† Reference 8.

appears to be identical in both the quiescent and forced convective environments.

To investigate further the influence of forced convective motion on flame propagation *below the critical flow velocity*, a limited number of surface-temperature-profile measurements were made (at least three tests were performed at each of four values of U) using the techniques reported in Ref. 1, with PMM in 46% O_2, 54% Ar. Experimentally, δ was found to vary with U in a way that can be correlated by the empirical power law $\delta \propto U^{-1/3}$. For this result to be consistent

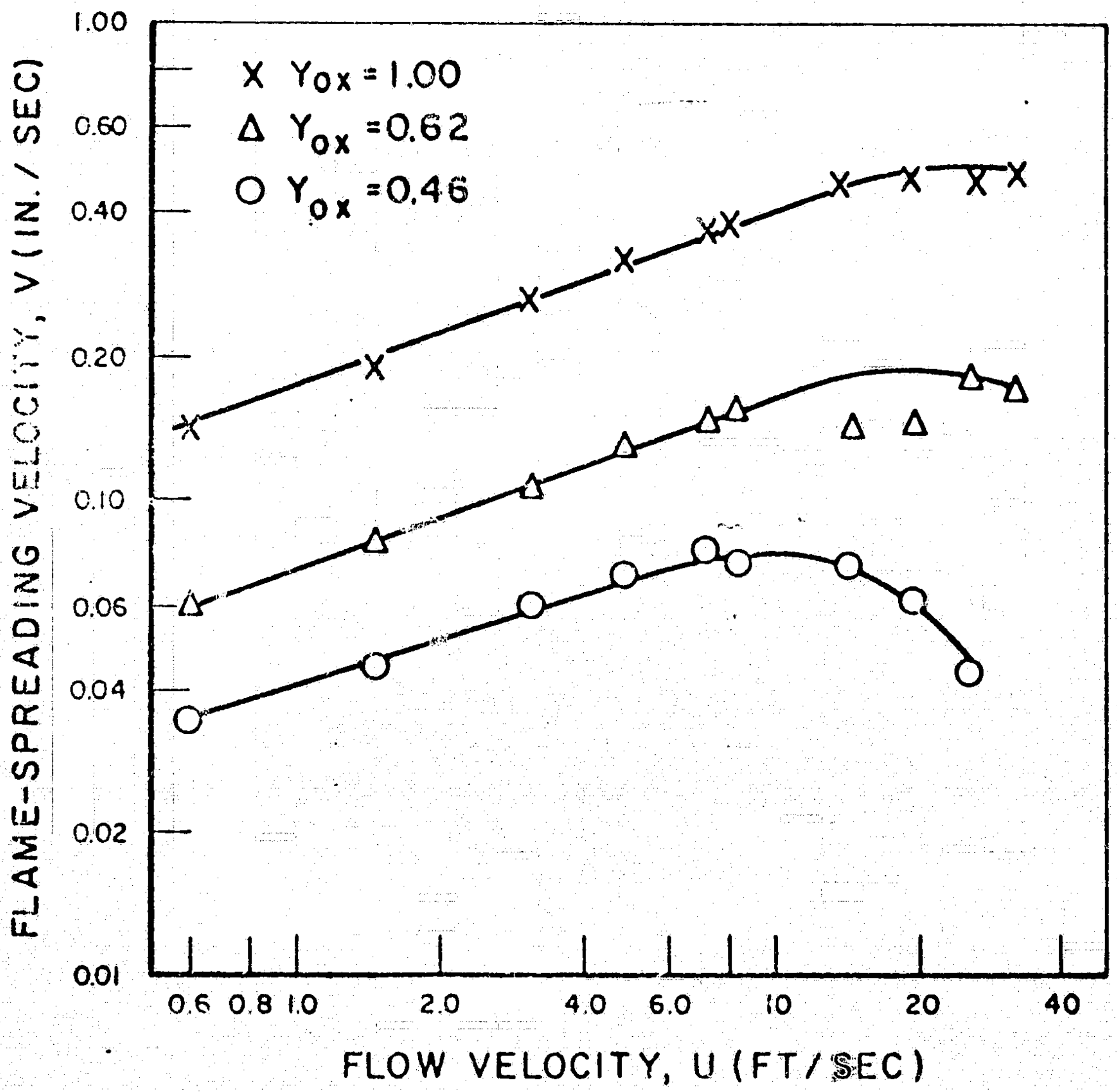


FIG. 7. V vs U for thick polymethylmethacrylate specimens in O_2/N_2 environments.

with the observed flame-spreading dependence on flow velocity and Eq. (6), $\dot{Q}_s$ is required to be essentially independent of the flow velocity. Results from the numerical work demonstrated this fact.[4]

Summary

Attention was focused on a small ignition region at the leading edge of the spreading flame. Algebraic relationships were developed which were more successful than previously developed expressions[1–3] in explaining a variety of experimentally observed phenomenon. It is concluded that processes occurring in the ignition region are of paramount importance in the flame-spreading phenomenon and that the role played by the solid phase in the over-all flame-spreading mechanism is generally understood, but the gas-phase processes require further definition.

Acknowledgments

The authors thank J. H. Royal for obtaining the cellulosic flame-spreading data and P. R. Bhat for obtaining the initial temperature data.

This work was supported by NASA Grant NGR-31-003-014.

REFERENCES

1. McAlevy, R. F., III and Magee, R. S.: *Twelfth Symposium (International) on Combustion, p. 215*, The Combustion Institute, 1969.
2. de Ris, J. N.: *Twelfth Symposium (International) on Combustion*, p. 241, The Combustion Institute, 1969.
3. Sanchez Tarifa, C., Perez del Notario, P., and Munoz Torralbo, A.: *Twelfth Symposium (International) on Combustion*, p. 229, The Combustion Institute, 1969.
4. Lastrina, F. A.: "Flame Spread Over Solid-Fuel Beds, Solid- and Gas-Phase Energy Considerations," Ph.D. thesis, Stevens Institute of Technology, June, 1970.
5. Magee, R. S.: "The Mechanism of Flame Spreading Over the Surface of Igniting Condensed Phase Materials," D.Sc. thesis, Stevens Institute of Technology, 1968.
6. Waldmen, C. H., Cheng, S. I., Sirignano, W. A., and Summerfield, M.: Theoretical Studies of Diffusion Flame Structures, AMS Report No. 860, AFOSR Contract AF 49(638) 1267, Jan. 1969.
7. McAlevy, R. F., III, Magee, R. S., Baham, P. M., and Lastrina, F. A.: "Some Recent Experimental Observations on Flame Spreading Over Solid Fuel Surface," presented at the 1969 Fall Meeting, Western States Section, The Combustion Institute, 27–28 Oct., LaJolla, California.
8. McAlevy, R. F., III: "The Investigation of Flame Spreading Over the Surface of Igniting Solid Propellants," Quarterly Report, NASA Grant NGR-31-003-014, ME-RS 69009, Stevens Institute of Technology, Hoboken, N. J. (July, 1969).
9. Carslaw, H. S. and Jeager, J. C.: Conduction of Heat in Solids, 2nd ed., Oxford at the Clarendon Press, 1959.
10. Huggett, C., von Elbe, G., and Haggerty, W.: The Combustibility of Materials in Oxygen-Helium and Oxygen–Nitrogen Atmospheres, Brooks Air Force Base, Report SAM-TR-66-85, Dec. 1966, prepared by Atlantic Research Corp.
11. Kwentus, G. K.: "Fuel Preheating in Free-Burning Fires," Ph.D. thesis, Massachusetts Institute of Technology, 1967.
12. Bhat, P. R.: "Influence of Initial Fuel Bed Temperature on Flame Spreading Velocity," Masters thesis, Stevens Institute of Technology, 1970.
13. Murty, K. A. and Blackshear, P. L., Jr.: "An X-Ray Photographic Study of the Reaction Kinetics of α-Cellulose Decomposition," Western States Section, The Combustion Institute, April 1966.

COMMENTS

J. de Ris, Factory Mutual Research Corp. It is indeed fortunate that we now have experimental measurements for flame spread over thermally thin and thick materials of the same chemical composition over wide ranges of ambient oxygen concentration and pressure. These results can be compared to the thermally thin and thick theories presented at the previous Symposium. These theories postulated that the flame-spread mechanism over solid fuels is controlled by forward conductive heat transfer through the gas phase. It was shown that the forward heat conduction through the solid phase does not influence the flame-spread rate for a thermally thick fuel bed. By postulating that the gas-phase reaction kinetics are infinitely fast, and therefore not controlling, it was possible to solve the associated mathematical models, provided one assumes constant density, transport properties and uniform velocity profile.

The thin fuel-bed solution for the spread velocity V is

$$V \simeq (\sqrt{2}\lambda/\rho_w C_{pw}\tau) \times \{[T(\text{flame}) - T(\text{vap})]/[T(\text{vap}) - T_\infty]\},$$

where τ is the fuel-bed half-thickness and subscript w stands for the solid phase. Correspondingly, for a thermally thick fuel bed, we have

$$V = V_a(\rho C_p\lambda/\rho_w C_{pw}\lambda_{wy}) \times \{[T(\text{flame}) - T(\text{vap})]/[T(\text{vap}) - T_\infty]\}^2,$$

where

$$V_a \simeq \{\lambda g[T(\text{flame}) - T_\infty]/\rho C_p T_\infty\}^{1/3}$$

is the effective gravitationally induced gas-phase velocity evaluated one characteristic gas-phase length $2\lambda/(\rho C_p V_a)$ above the fuel bed. λ_{wy} is the fuel-bed thermal conductivity normal to the surface.

The thin fuel-bed formula predicts a spread rate independent of both the opposing gas velocity V_a and the pressure; however, the spread rate does increase with the adiabatic stoichiometric flame temperature $T(\text{flame})$. The thick fuel-bed result is quite different. In this case, the spread velocity is proportional to V_a, so that in a quiescent environment with gravity, the spread rate is proportional to the two-thirds power of pressure. As explained in the previous Symposium, one can predict the thick fuel-bed velocity using the thin fuel-bed formula, and estimating the depth of heat penetration τ_{si} into the solid phase beneath the flame.

The data taken by Royal and reported by Lastrina and Magee are correlated in Fig. A. The coordinates are chosen so that both the thin and thick fuel bed data should correlate if the theories are valid. The ordinate is proportional to the spread velocity, while the abscissa is proportional to pressure. The thermal properties for the solid phase correspond to those selected by Parker,[1] who also considered the downward burning over white index cards. The thermal conductivity of the cards was estimated on the basis of Parker's measurement of the density. The thermal properties of the gas phase were arbitrarily selected to be those of nitrogen at the vaporization (i.e., pyrolysis) temperature of the cards. The flame temperatures were selected on the basis of the flame-gas specific enthalpies, which provide a better measure of the gas-phase heat transfer. These enthalpy differences are indicated by $C_p[T(\text{flame}) - T(\text{vap})]$. The specific choices of property values do not influence the shape of these curves; they influence only the relative positions.

One sees that the correlation is indeed excellent, especially for oxygen mole fractions X_{O_2} greater than 21%. The data for 21% O_2 has the correct shape, but is shifted downward and to the right.

These data lend powerful support to the two theories. This agreement suggests that gas-phase

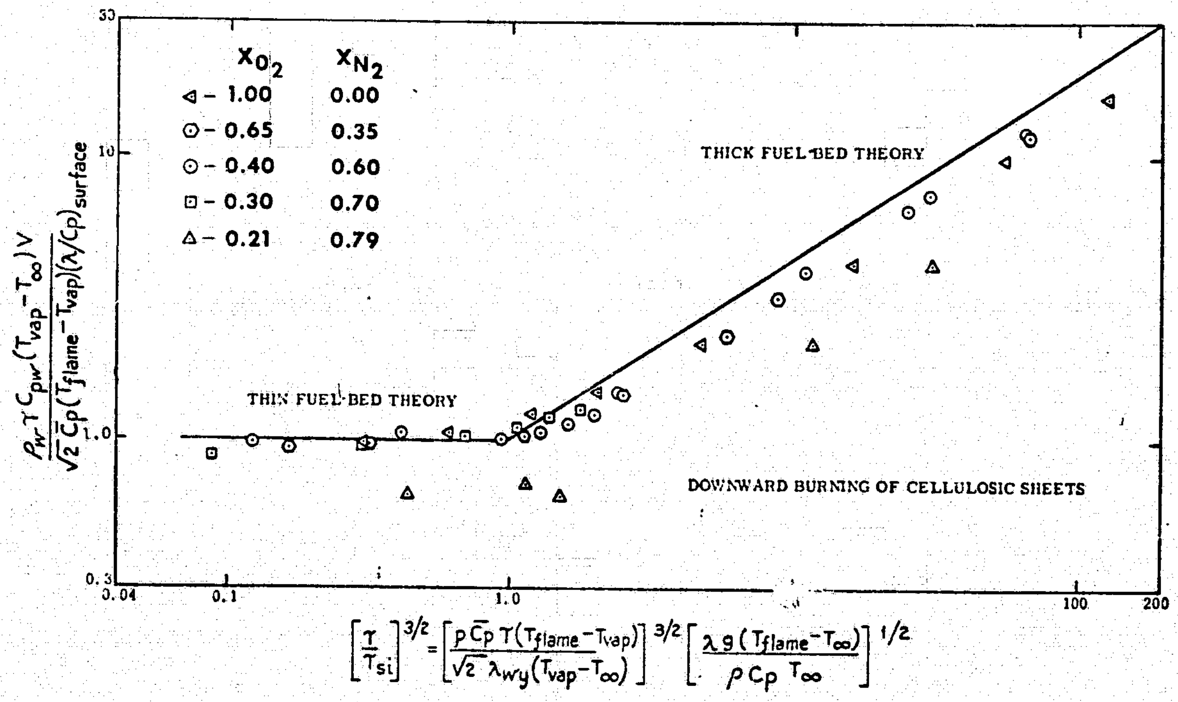


FIG. A

reaction kinetics is unimportant in the range of experimental conditions. However, one does anticipate that, as the pressure or oxygen concentration decreases there will be a marked drop in flame-spread rate due to reaction kinetics. This extinction point should be sensitive to small concentrations of gas-phase inhibitors.

Reference

1. Parker, W. J.: "Flame Spread Model for Cellulosic Materials," presented at the 1969 Centra-States Section, The Combustion Institute, University of Minnesota, March 1969.

Authors' Reply. Our simple derivation of flame-spreading velocity as a function of a variety of influential parameters results in the naturally occurring criterion [Eq. (4)] for discriminating between thermally "thin" and "thick" fuel beds, insofar as the flame-spreading characteristics are concerned. Different equations [Eqs. (17) and (18)] relating flame-spreading velocity and these parameters are required for the successful correlation of data in each region, as demonstrated herein. The model underlying the derivation is consistent with most of de Ris's comments concerning the details of the mechanisms operative during flame spreading.

Manipulation of our equations, incorporating de Ris's equation for V_a, permits evolution of the grouping of terms plotted as the coordinates shown on the figure accompanying his comment, and hence the exact shape of the curve as well.

Assuming the terms $Q_c/CY_{\text{ox}}F(PY_{\text{ox}})$ are proportional to $T_f - T_b$, and making this substitution in Eqs. (17) and (18), yields

$$V' \propto K(T_f - T_b)/\rho_s C_s \tau' (T_b - T_0) \quad (21)$$

and

$$V \propto K^2(T_f - T_b)^2/\rho_s C_s K_s \delta (T_b - T_0)^2. \quad (22)$$

The denominator in Eq. (4) is τ_{si}, so that

$$\bar{\tau} = \tau/\tau_{si} = \tau[(\rho_s C_s V)^{1/2}/(K_s \delta)^{1/2}]. \quad (23)$$

Recognizing our ignition region δ as de Ris's characteristic gas-phase length,

$$\delta = 2K/\rho C V_a, \quad (24)$$

where

$$V_a \simeq \{Kg(T_f - T_0)/\rho C T_0\}^{1/3}, \quad (25)$$

and substituting Eqs. (22), (24), and (25) into Eq. (23), yields

$$\tau/\tau_{si} \simeq [\rho C \tau (T_f - T_b)/2K_s(T_b - T_0)] \times \{Kg(T_f - T_0)/\rho C T_0\}^{1/3}. \quad (26)$$

The ordinate on Fig. A follows directly from Eq. (21), and the abscissa from Eq. (26).

PART III

THE MECHANISM OF FLAME SPREADING OVER THE SURFACE OF IGNITING, CONDENSED PHASE MATERIALS

Reprinted from

Twelfth Symposium (International) on Combustion

Union Trust Bldg. Pittsburgh, Penna.

PRINTED IN THE UNITED STATES OF AMERICA

N71-31429

THE MECHANISM OF FLAME SPREADING OVER THE SURFACE OF IGNITING CONDENSED-PHASE MATERIALS

ROBERT F. McALEVY, III AND RICHARD S. MAGEE

Combustion Laboratory, Stevens Institute of Technology, Hoboken, N. J.

This paper describes an experimental and theoretical investigation of the fundamental mechanism by which a flame spreads over the surface of a condensed-phase material in a quiescent gaseous environment containing a component with which it can react chemically. It is postulated that the advancing flame vaporizes the surface material lying before it. As these vapors diffuse away from the surface, they undergo an exothermic reaction with the chemically active component in the gaseous environment, and ignite; thus, flame spreading is viewed as continuous diffusive, gas-phase ignition.

Flame-spreading velocities have been measured for a variety of solid materials in O_2/inert environments between 4 and 415 psia. Well-defined experimental conditions yielded reproducible results, and thus suggest that flame-spreading velocity is an intrinsic combustion quantity. All data can be correlated by a power-law relationship between the flame-spreading velocity (V) and two gas-phase parameters—pressure (P) and reactive component mole fraction (Y_{ox})—in the form

$$V \propto (PY^{m}_{ox})^{\Phi}.$$

It is concluded that V is controlled by a gas-phase physical process—probably either heat or mass transfer—which supports the mechanism proposed.

Temperature distributions ahead of the propagating flame were obtained from surface-mounted, fine-wire thermocouples. The temperature level as the flame passes over the thermocouple bead is independent of P, Y_{ox}, and inert diluent, and about 120° C below that measured previously during steady-state vaporization. Thus, it is concluded that direct surface attack by oxygen is unimportant during flame spreading and that the transient vaporization phenomenon is probably quite different than that of steady pyrolysis.

The mathematical statement of the postulated flame-spreading mechanism is sufficiently complex that a complete analytical solution is currently impossible. Postponing numerical solutions, simplistic analyses were conducted that resulted in predicted flame-spreading characteristics that were well supported by the data obtained over the entire range of experimentation. Based on the evidence presented, the authors conclude that the postulated theory is probably valid, and engineering design of systems involving flame-spread control now can be put on a rational basis.

Background and Introduction

Flame spreading is an important factor in the ignition of solid-propellant and hybrid rocket motors, fires in manned spacecraft, building fires, and forest fires. However, the basic mechanism of flame spreading has been unknown, and thus various attempts to control flame-spreading rate necessarily had to proceed on an empirical basis. The subject research program was designed to produce a fundamental understanding of the flame-spreading process with the ultimate objective of providing a rational basis for controlling fire spread.

Observation of flame spreading during solid rocket motor ignition was reported by Parker *et al.*[1] who postulated successive ignition of local portions of the propellant surface as a result of convective heating. Barrere and Moutet[2] obtained an empirical correlation of the rate of combustion chamber pressure rise and flame-spreading rate during the ignition transient in a hybrid-rocket motor, but did not arrive at a fundamental understanding of the process. Recent tragedies involving fires in oxygen-rich, manned space capsules have focused attention on the fire hazards associated with such atmospheres.[3] However, the mechanism of rapid flame spreading under such conditions was not considered in arriving at suggested design modifications,[4] so the proposed design changes for improved safety could not have been based on rational criteria concerning flame spreading—and, consequently, they probably are not as effective as others that are available within the same framework of constraints.

In a recent survey of the field, it was concluded that the present level of understanding of fire spread in buildings and forests lies somewhere between a qualitative description of the phenomenon and an empirical correlation of data.[5] It appears that, for example, an essential first step for the prediction of the rate of spread of fire through a building is the description of the mechanism of flame propagation over the surface of the various building materials.

Although there have been many investigations of the solid-fuel or solid-propellant ignition process in gaseous oxidant environments, and a number of practical flame-spreading studies,[1,2,6–8] there appears, with the exception of the work produced in the authors' laboratory, to be only one previously published theoretical investigation of the basic mechanism by which a flame spreads over such surfaces once ignition occurs.[9] Tarifa and Torralbo[9] have produced an analysis in which the flame propagation velocity was calculated by assuming that the flame reaches a certain location when the temperature of the fuel surface at that location reaches an "ignition temperature." Heating of the fuel ahead of the flame is treated by considering radiative heat transfer from the flame burning at surface locations already ignited to those being ignited, and two-dimensional heat conduction within the fuel.[9] This thermal theory neglects interdiffusion of fuel and oxidant vapors, a process believed important by workers in this laboratory.[10] More recently, Friedman also suggested that the diffusion process must be included in any complete model.[11]

Workers in this laboratory have proposed a theory of flame spreading that views the process as continuous, diffusive gas-phase ignition.[10] Evidence from a number of sources has led the authors to postulate that the principal exothermic chemical reaction of importance in flame spreading takes place in the gas phase.[10] Therefore, vapors emerging from the condensed-phase material must be transported to this site in order for the reaction to take place. Heat required for vaporization of the condensed-phase material is supplied by the advancing flame and by feedback from the exothermic gas-phase reaction. The first mathematical analysis of this phenomenon was produced after making extensive simplifying assumptions. Nevertheless, it resulted in a predicted power-law dependence of flame-spreading velocity upon environmental pressure and reactive component mole fraction that was generally supported by data obtained for a wide variety of solid materials (e.g., thermoplastics, solid-rocket propellants, and an inorganic oxidant), albeit over a very narrow range of experimental parameter variation.[10] Improved analysis followed.[12,13] These will be reviewed in the Theory section and discussed in the Results and Conclusions section.

Previous experimental studies were conducted at atmospheric pressure and below in oxygen–nitrogen environments.[10] The subject results were obtained over a much-expanded pressure range (up to 415 psia) and the inert diluent was varied to include helium and argon in addition to nitrogen. This large variation of the thermodynamic and transport properties of the environment was made to permit more-comprehensive testing of the power-law prediction, and better assessment of the importance of mass and heat transfer in the flame-spreading process. Also, temperature distributions ahead of the spreading flame were obtained from surface-mounted, fine-wire thermocouples. These data were incorporated in the prediction of flame-spreading-velocity characteristics as well as employed diagnostically to determine the nature of the heat transfer from the advancing flame to the surface before it and the response of the surface to the transient heating.

Experimental Approach

Flame-Spreading-Velocity Measurement

The flame-spreading velocity over the surface of various thermoplastics and solid-rocket propellants was measured in quiescent environments of various pressures and compositions. Small test specimens (3 in. × 0.375 in. × 0.125 in.) were mounted, smooth 3 in. × 0.375 in. surface upwards, on backing plates (3.25 in. × 0.5 in.) and burned in a relatively large test chamber (10 in. i.d. × 18 in.) fitted with an observation window (Fig. 1).

Pressure increase in the chamber during flame spreading was reduced to a negligible level by connecting a large surge tank (10 cu. ft.) to the test chamber. A one-way valve was inserted between the chamber and the surge tank. In preparing to run at a selected pressure, the surge tank was first pressurized to that level with compressed air. After placing a mounted specimen in the chamber, 3 in. × 0.375 in. surface upward, the chamber was sealed and then evacuated and charged with the selected test gas to the pressure in the surge tank, thus opening the check valve.

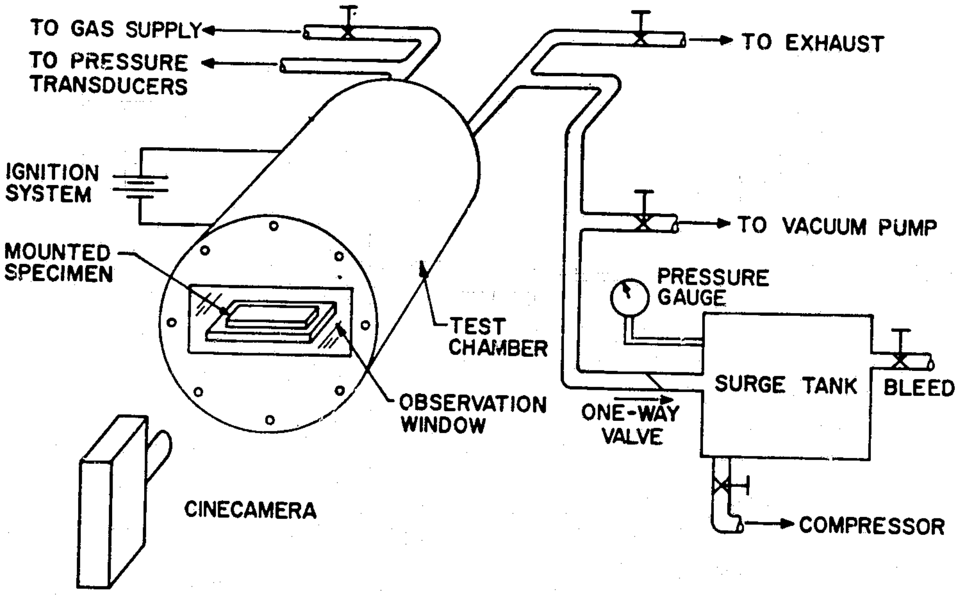


FIG. 1. Schematic of apparatus for flame-spreading-velocity measurement.

The chamber gas was allowed to become quiescent before igniting the specimen. This approach eliminated complications of the flame-spreading process of forced convection; and minimized the complication of free convective effects, inextricably linked to the spreading wave itself, that nearby objects would produce.

The specimens were ignited by an electrically heated wire positioned along the 0.375 in. edge on the top surface. In order to insure uniform and simultaneous ignition across this edge of the specimen, it was necessary to fasten the ignition wire to the surface with plastic cement. To prevent the flame from spreading too rapidly along the 3 in. edges of the specimen—a phenomenon that takes place faster than flame spreading over the top surface, and therefore one that could result in spuriously higher measured values of the latter process—it was necessary to inhibit the edges of the specimen. An inorganic compound, Sauereisen Insa-Lute Adhesive Cement, No. 1 paste, was applied to the sides and extended over the 3 in. edges and onto the top surface for a distance of about 1/32 in.

Flame spreading data were obtained for high spreading velocities from cinecamera records. Low spreading velocities (below about 0.1 in./sec) were determined from stop-watch measurements of the time required for the flame to propagate a fixed distance (2 in.). For those events recorded photographically, Kodak Tri-X 16-mm film and a Bell and Howell 16-mm, Model 70-D1 cinecamera were used. The film was exposed at a calibrated rate between 24 and 71.6 frames/sec, the higher rates being used for the higher flame-spreading velocities. From the developed film, flame-spreading velocity was determined using a motion analyzer (Vanguard, Model M-16) to measure the distance propagated during the known time between selected frames. The spreading velocity was found to accelerate immediately after ignition, reaching an apparently steady value after the flame had spread over about 0.5 in. of the specimen surface. Only the steady values of flame-spreading velocity were recorded and reported herein.

Surface-Temperature-Profile Measurement

Surface-temperature profiles ahead of the propagating flame were obtained for two thermoplastics (polystyrene and polymethylmethacrylate). To discern accurately the nature of the temperature profile, it was necessary to employ extremely fine thermocouples (7.6-μ-diam wire, 15-μ-diam bead, Pt/Pt–10% Rh). These were fabricated by the authors. The thermocouple-mounting procedure was as follows: The surface of the specimen was moistened with a solution of the thermoplastic in methylethylketone, and the bead carefully positioned approximately two-thirds the distance from the ignition wire, with the leads extending to the far end of the specimen. Once the solution dried, the specimen was viewed under a high-power microscope to ascertain that the thermocouple was firmly affixed to the specimen surface.

The thermocouple signal was fed into a high-impedance amplifier (Honeywell Model 104 Accudata DC Amplifier). The amplifier signal was fed into a continuously recording galvanometer (Honeywell Model 906C Visicorder Oscillograph). As the flame passed over the bead, a history of thermocouple-output voltage was pro-

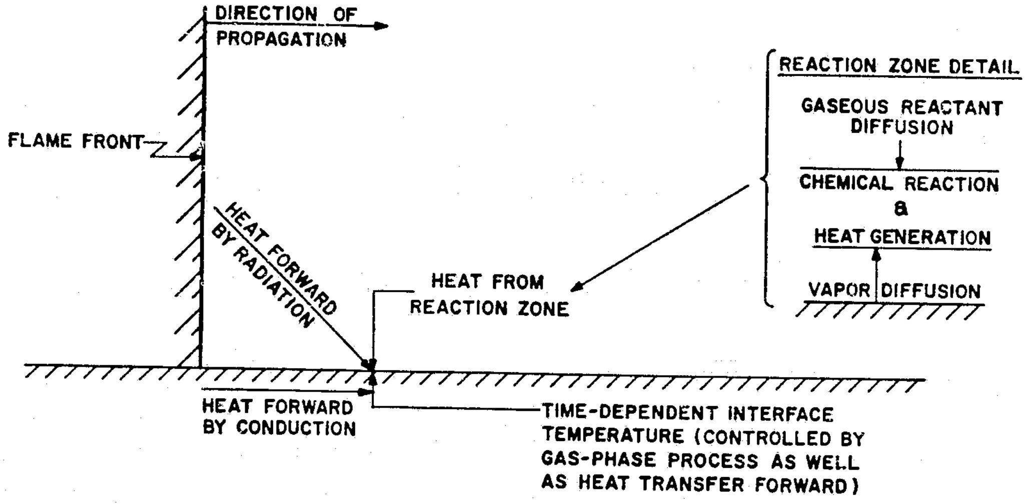


FIG. 2. Processes involved in continuous diffusive gas-phase ignition model of flame spreading.

duced. The recorder-chart speeds employed were 2, 10, and 50 in./sec, depending upon the flame-spreading velocity. Knowledge of the flame-spreading velocity permitted the histories to be converted to spatial distributions.

The recorder was calibrated by means of a precision potentiometer. Assuming the thermocouple characteristics were represented by those given in National Bureau of Standards Circular No. 561, temperature profiles were obtained.

Theory

The theory is proposed with the intent of describing the phenomenon of flame spreading over the surface of a condensed-phase material in a gaseous environment containing a component with which it can react chemically. Evidence from a number of sources has led the authors to believe that the principal exothermic chemical reaction of importance in flame spreading takes place at a site in the gas phase.[10] Therefore, vapors emerging from the condensed-phase material must be transported to this site in order for the reaction to take place. Heat required for vaporization of the material is supplied by the advancing flame. The processes involved are depicted schematically in Fig. 2.

Ignition starts at a certain surface location in advance of the flame when it experiences a temperature increase due to the approaching flame; at a sufficiently high temperature the surface pyrolyzes and emits vapors. As the vapors diffuse away from the surface, they react chemically with the active component in the environment, liberating heat and increasing the local temperature and, hence, the heat feedback to the surface. The advancing flame, having now moved closer to this location of interest, further accelerates the vaporization rate and thus the vapor-transport rate; the heat-release rate is continually accelerated by the increasing vapor-flow rate to the site of active chemical reaction, leading to a temperature "run-away" to ignition. Ignition occurs just as the flame reaches the location. Thus, flame spreading is postulated to be a process of continuous, diffusive, gas-phase ignition.

This mechanism of flame spreading is believed to be valid whether or not the surrounding environment is in motion. However, during the subject program, the investigation was limited to consideration of the process in a quiescent environment in order to reduce the complexity of mathematical analyses. (As outlined in Ref. 10, historical precedent for considering the quiescent situation first is found in the development of the gas-phase theory of solid-fuel ignition by a hot oxidant-containing gas.) Even so, the equations for conservation of mass and energy required to completely describe flame spreading in a quiescent environment take the form of a set of four, unsteady, very nonlinear, two-dimensional, coupled, partial-differential equations. A complete solution should result in an eigenfunction for the flame-spreading velocity. (Since the phenomenon of interest involves heat transport in a principal direction that is normal to the principal direction of mass transport, their complete solution would be materially more difficult than, for example, the solution of diffusive, gas-phase ignition of a condensed-phase material by a hot gas containing a reactive component, where heat and mass transfer occur in parallel directions.[14]) It appears that a complete analytical solution is currently impossible, and expensive numerical solutions have been postponed pending further verification of the mechanism proposed. In their place, simplistic analyses have been performed[10,12,13] in order to produce predictions of flame-spreading velocity within the compass of the proposed theory. These will be reviewed briefly.

The principal assumption that flame spreading is continuous, diffusive, gas-phase ignition, is expressed mathematically as

$$V = \delta / t_{ig}, \tag{1}$$

where V is the flame-spreading velocity; δ is the distance along the surface of the condensed-phase material that is affected by the presence of the flame (this quantity was determined experimentally, which allowed the gas-phase-energy equation to be "uncoupled" from the solid-phase-energy equation and resulted in a noneigenfunction solution); t_{ig} is the time between the instant at which the advancing flame first produces a significant effect at a location on the surface and the instant at which ignition occurs in the gas phase above that location (this quantity was obtained from various solutions of the one-dimensional, unsteady conservation equations in the gas phase, as discussed below).

The analyses produced[10,12,13] were all designed to obtain a prediction of t_{ig}, and were all based on a number of common subsidiary assumptions concerning the elementary processes involved. For example, it was assumed that: mixing takes place by molecular interdiffusion; gas-phase chemical reaction is second order, and occurs at a rate described by the Arrhenius expression; density, specific heat, transport properties, etc., were constant; consumption of gas-phase reactant and diffusing vapors is negligible during ignition, which allows "uncoupling" of their mass-conservation equations from the gas-phase energy equation; and, in Refs. 10 and 12, a "zeroth-order" solution was obtained by integration of the gas-phase-energy equation. Finally, since the pivotally important boundary condition—the vaporization response of the surface to transient heating—is currently unknown for all materials, it was necessary to make a heuristic assumption: that the surface-vaporization rate has a power-law dependence upon time throughout the ignition period.

(Only experiments performed in oxygen–inert mixtures are reported on herein, so the mole fraction of reactive gas-phase component will be designated by Y_{ox}. However, the theory is not restricted to solid fuels and gaseous oxidants—it is equally valid for the inverse situation.)

All the analyses have resulted in a predicted power-law dependence of t_{ig} upon environmental pressure (P) and gas-phase reactive component mole fraction (Y_{ox}), that can be represented as

$$t_{ig} \propto (P Y^{s}_{ox})^{-\beta}, \tag{2}$$

where the values of s and β depend upon the detailed nature of the particular assumptions made in the different analyses. Nevertheless, in all cases, β was predicted to be relatively independent of the environmental gas composition, but sensitive to the transient vaporization characteristics of the condensed-phase material, while s was predicted to be independent of the transient pyrolysis process (and therefore, presumably, the nature of the condensed-phase material), but strongly dependent upon the nature of the inert diluent.

Substituting (2) into (1) yields

$$V \propto \delta (P Y^{s}_{ox})^{\beta}. \tag{3}$$

In order to produce a meaningful prediction of V, it is necessary to know $\delta = \delta(P, Y_{ox})$. Experimental results to be presented in the next section indicate that this function can be represented in the form

$$\delta \propto (P Y^{q}_{ox})^{-r} \tag{4}$$

then

$$V \propto V(P, Y_{ox})$$

becomes

$$V \propto (P Y^{m}_{ox})^{\Phi}, \tag{5}$$

where

$$\Phi = \beta - r \tag{6}$$

and

$$m = (s\beta - rq)/(\beta - r). \tag{7}$$

Results and Conclusions

Flame-spreading velocity was measured for two types of nitrate ester propellants, here referred to as Propellant A and Propellant B, (obtained through the kindness of J. P. Picard, R. G. Wetton, and R. F. Jasinski of the Propellant Laboratory, Feltman Research Laboratory Division, Picatinny Arsenal, Dover, N. J.), and two thermoplastics that are typical of composite propellant fuel-binders, polystyrene (PS) and polymethylmethacrylate (PMM). The propellants were tested in mixtures of oxygen (O_2) and nitrogen (N_2), and the thermoplastics in mixtures of O_2 and N_2, O_2 and argon (Ar), and O_2 and helium (He)—of various levels of oxygen mole fraction (Y_{ox}) and total pressure (P). Surface-temperature profiles ahead of the advancing flame were obtained for PS in O_2 and for PMM in mixtures of O_2/N_2, O_2/Ar, and O_2/He at various levels of Y_{ox} and P. This section is organized in segments in which, successively, some results and then conclusions based on those results are presented.

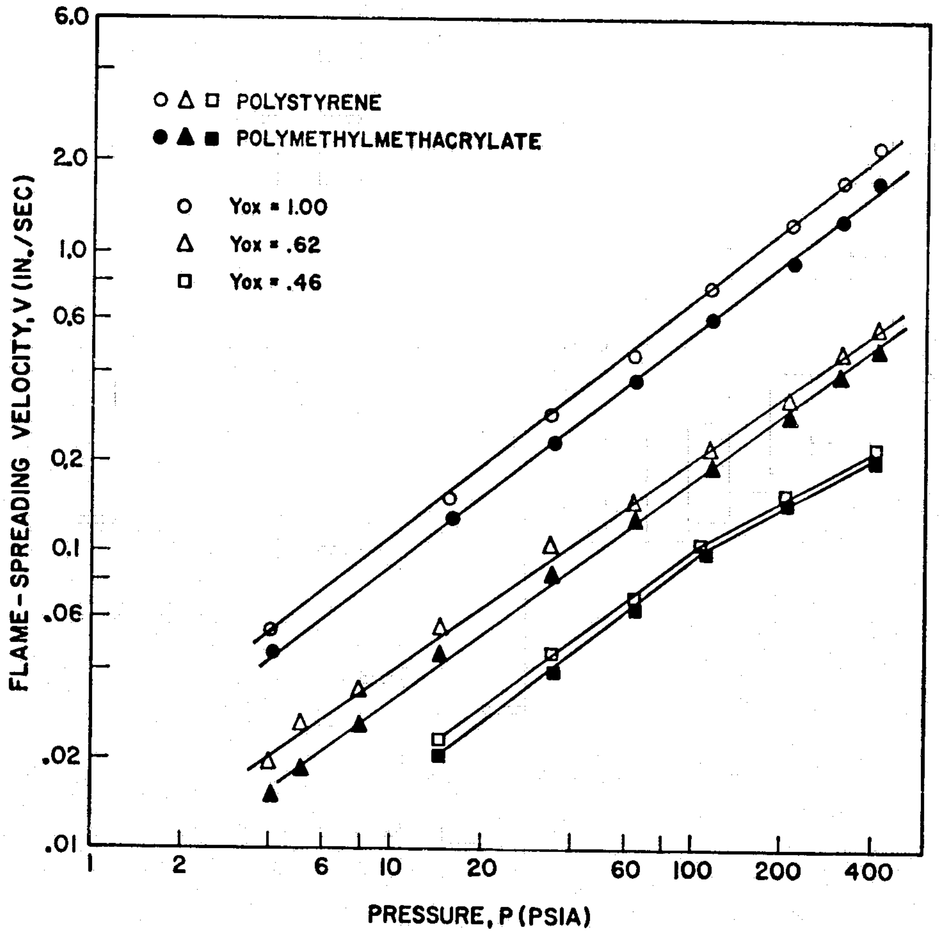


FIG. 3. Log V vs log P for two thermoplastics in O_2/N_2 environments.

A. The experimental approach employed resulted in a spreading flame that was in all cases well defined, propagated uniformly after being established, and remained perpendicular to the long side of the specimen during its transit. With few exceptions, all data were within ±5% of the arithmetic mean values shown on the accompanying figures.

Thus, it is concluded that when specimens are prepared with care and experimental conditions are well defined, a reproducible flame-spreading velocity can be measured that is an intrinsic combustion property of the particular system. That is, the flame-spreading velocity over the surface of a condensed-phase material in an environment containing a component with which it can react chemically appears to be a property analogous to the laminar flame velocity in gaseous combustible systems. In both cases, measured velocities are influenced by experimental apparatus, size of test specimen, and conditions of test—including initial temperature and motion in the environment. These influences on flame-spreading-velocity measurements are currently under study in this laboratory. (Failure to control experimentally such influences, including specimen preparation and mounting, led to large scatter in the data previously obtained by others[11] and so the intrinsic nature of the flame-spreading velocity was not discovered.) It is recognized that the values for V obtained by the authors reflect the particular experimental approach employed. However, the low data scatter and smooth dependence of V upon P and Y_{ox} suggest that the factors influencing flame spreading in the subject experiment will be common to all well-defined experiments.

B. All the data obtained to date in the authors' laboratory, which involves over 1500 experiments performed with solid ammonium perchlorate in a fuel gas environment,[10] composite solid propellants in chemically reactive environments, and the subject data with nitrate ester solid propellants and thermoplastics, can be correlated by a power-law relationship between V and two gas-phase parameters P and Y_{ox}. (Discussion of the distinction between propellant normal deflagration and surface flame spreading appears in Ref. 15.) Specifically, the influence of P on V for the two thermoplastics for various values of Y_{ox} in O_2/N_2 and O_2/He environments is shown in Figs. 3 and 4, respectively. The measured flame-

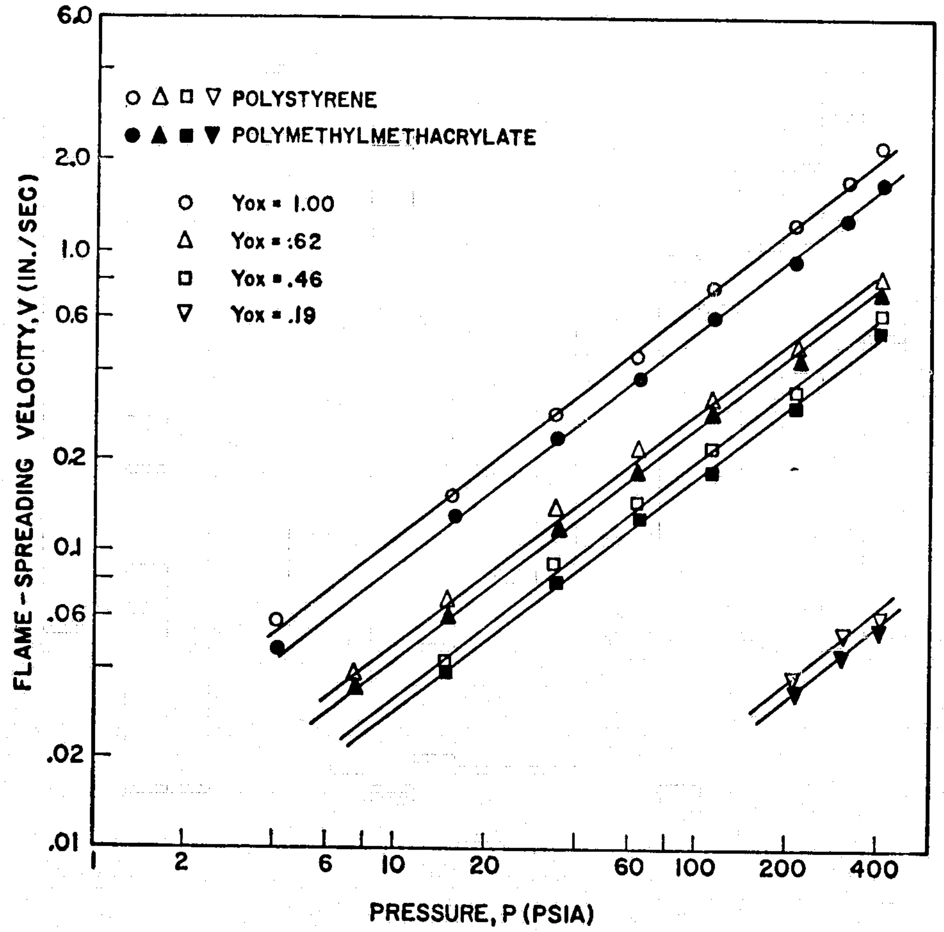


FIG. 4. Log V vs log P for two thermoplastics in O_2/He environments.

spreading velocity in all cases could be correlated, over a pressure range of 400 psia, with the test-gas environmental parameters Y_{ox} and P (see Figs. 5 and 6) in the form

$$V \propto (PY^{m}_{ox})^{\Phi},$$

which is identical to Eq. (5). The nitrate ester propellant data could also be correlated by this equation over the same pressure range. Experimentally determined values of Φ and m are shown in Table I.

Due to the fact that the systems tested had widely varying chemical properties, a general conclusion can be drawn from the successful correlation of all these data by the same equation: V is controlled by a common, gas-phase, physical process—probably either heat or mass transfer. [However, it is possible to draw implications concerning important chemical processes as well. For example, the vapors emitted from the surface of the nitrate ester propellants contain both fuel and oxidant components, while those coming from the surface of a thermoplastic contain only fuel. Nevertheless, the flame-spreading characteristics in oxygen-containing environments are well represented by Eq. (5) for both materials. This implies that, for the conditions tested, the propellant fuel vapors react more vigorously with the oxygen of the environment than with the oxidant component of the emitted vapors.]

C. Over 200 surface-temperature profiles were obtained from PMM in various oxygen–inert diluent mixtures. A typical surface-temperature profile is shown in Fig. 7. The distance ahead of the flame substantially affected by the presence of the flame was extracted from these profiles. Since the surface temperature is a continuously varying function of the distance ahead of the flame, it was necessary to be arbitrary in characterizing the distance "substantially affected." The distance over which the surface temperature grows from 10% to 90% of its final value was selected for this purpose and defined as δ^* (Fig. 7). Inspection of the profiles revealed that δ^* was a function of P, Y_{ox}, and type of diluent that could be represented as $\delta^* \propto (PY^{q}_{ox})^{-r}$, with the values of r and q given in Table II.

Thus, the use of Eq. (4) in the Theory section is justified—and this empirical information, in combination with the results of the analyses that

2⊕

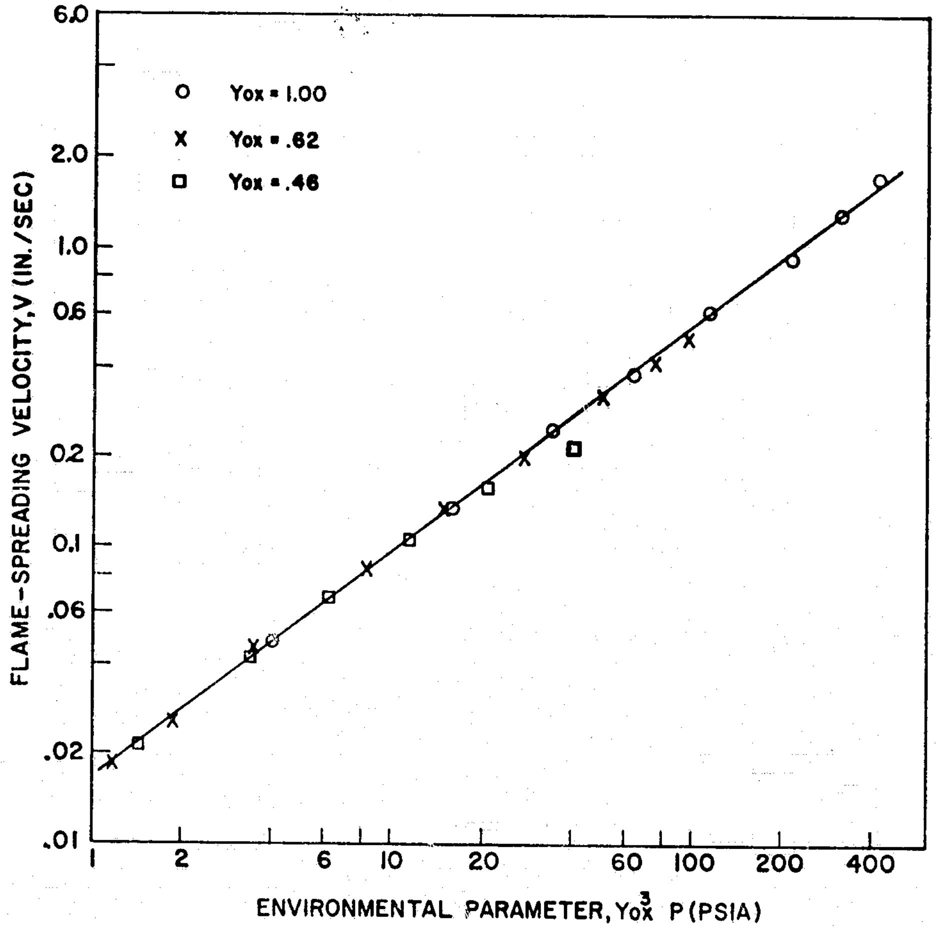


FIG. 5. Log V vs log Y^3_{ox} P for polymethylmethacrylate in O_2/N_2 environments.

yielded Eq. (2), yields Eq. (5), which as stated above, permits excellent correlation of all data obtained to date.

D. It was found that m is a function of diluent gas and type of specimen, either thermoplastic or solid propellant, while Φ, although dependent upon the type of specimen, is relatively insensitive to the diluent gas (see Table I). The theoretical analysis predicts that $\Phi = \Phi(\beta, r)$ and $m = m(s, \beta, r, q)$.

Therefore, qualitative predictions regarding Φ and m can be made from qualitative information of the quantities s, β, r, q. Table II indicates that r is only somewhat dependent, while q is strongly dependent, upon the inert diluent in the environmental test gas. Also, as stated in the Theory section, β should be sensitive to the pyrolysis characteristics of the specimen, but relatively independent of the environmental gas composition, while s is strongly dependent upon the inert diluent.

Thus, the theoretical analysis predicts that Φ should be dependent upon type of specimen, but only slightly sensitive to environmental test gas, while m should be a function of both inert diluent and type of specimen. The experimental findings, as stated above and listed in Table I, support these qualitative predictions.

E. Values of Φ and m may be calculated from Eqs. (6) and (7) if the parameters s and β are known. Theoretically predicted values for s can be calculated on the basis of Eq. (19) of Ref. 13. Based on the heuristic assumption of a power-law increase of surface vaporization rate with time, Eq. (20) of Ref. 13 results in the prediction that $\beta < \frac{1}{3}$. Since $r > \frac{1}{3}$ empirically (Table II), Eq. (6) yields negative values of Φ, which is contrary to what is found experimentally.

Therefore, it is concluded that while the simplified analysis resulted in the correct prediction of a functional dependence of V upon P and Y_{ox}, and allows qualitative predictions to be made regarding Φ and m, it results in poor quantitative predictions. This failure could be caused by an error in the proposed theory or in the assumed boundary condition, or in an oversimplification in the analytical treatment, or, more probably, in some combination of these. In any case, an unequivocal assessment cannot be made at this time. More information is required.

F. For the heuristic assumption of constant surface-vaporization rate, a "zeroth-order" solu-

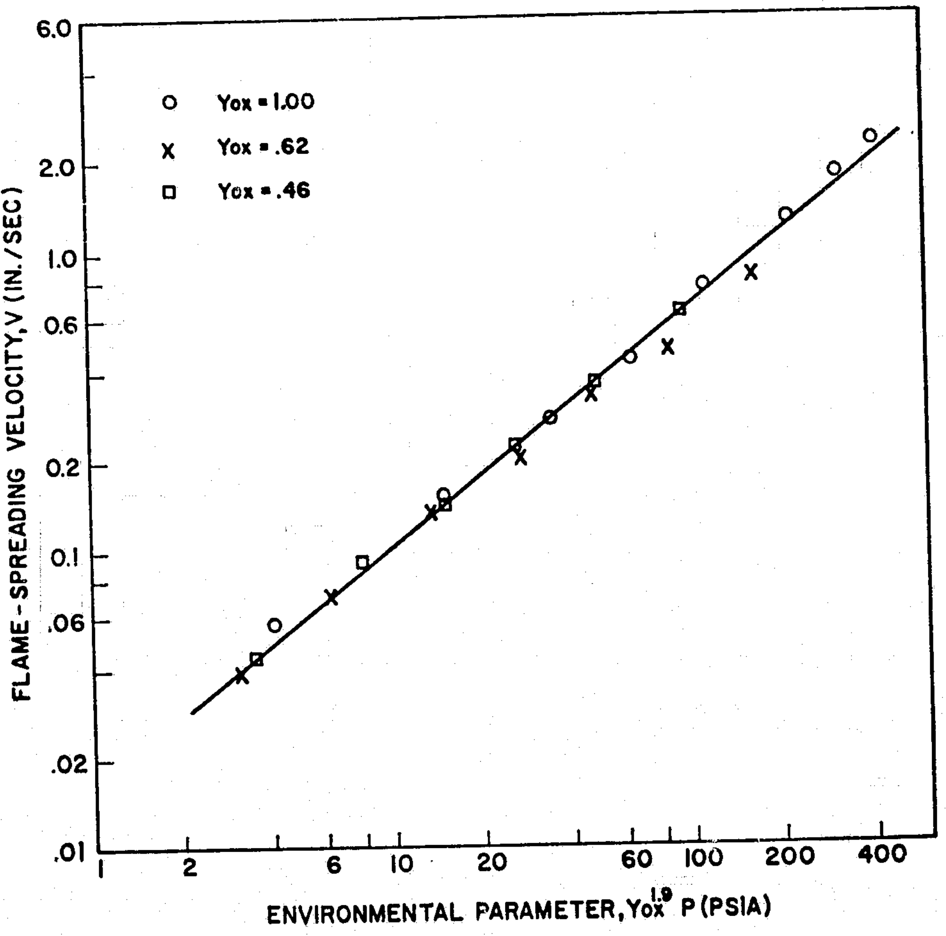


FIG. 6. Log V vs log $Y^{1.9}_{ox}P$ for polystyrene in O_2/He environments.

tion of the one-dimensional, unsteady conservation equations for diffusive, gas-phase ignition results in the prediction $t_{ig} \propto P^{-1.44}$, according to Ref. 16. The result of this analysis, i.e., $\beta = 1.44$, when employed in the calculation of m and Φ, yields the values displayed in Table III. The agreement between prediction and experiment is remarkably close. And further, if it is assumed heuristically that t_{ig} depends inversely upon Lewis Number, as suggested in the analysis on page 17 of Ref. 13, then the predicted value for m in the O_2/He environment becomes 1.6, and agreement is even better.

It is concluded that the previous failure in

TABLE I

Experimental values of Φ and m

	Environmental composition					
	O_2/N_2		O_2/He		O_2/Ar	
Specimen	Φ	m	Φ	m	Φ	m
Propellant A	0.62	2	—	—	—	—
Propellant B	0.65	2	—	—	—	—
Polystyrene	0.76	3	0.80	1.9	0.83	2.6
Polymethylmethacrylate	0.82	3	0.78	1.9	0.78	2.6

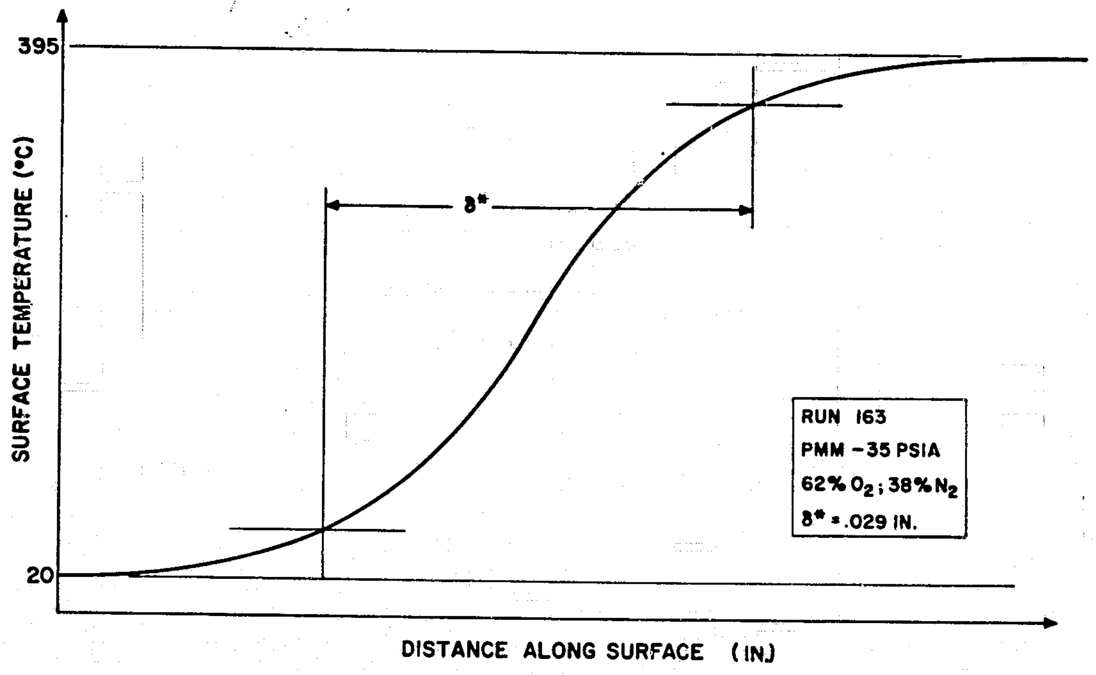


Fig. 7. Typical surface-temperature profile.

producing quantitative agreement between the predicted and experimentally determined power-law exponents was due to misrepresentation of the pivotally important boundary condition of surface-vaporization rate. The proposed theory and simplifying assumptions employed in producing the solutions appear to be valid. [However, it is recognized that, for certain experimental conditions, "uncoupling" the equations, etc., is not valid and numerical integration will have to be performed. Compare the solutions of Ref. 16 to Ref. 14, for example.]

The authors recognize that the success to date of the proposed theory of flame spreading is necessary, but not sufficient, for absolute proof of its validity. It is possible that other theories might also result in successful prediction of flame spreading characteristics. For example, although not pointed out by the authors of Ref. 9, the solid-phase thermal theory could yield a dependence of P, Y_{ox}, and inert diluent upon V, if their influence on surface heating by the flame (say by radiation) were properly taken into account. But since surface-heating effects have been incorporated empirically into the subject analysis, by substitution of Eq. (4) into Eq. (3), this suggested extension of the thermal theory will probably not yield closer prediction than the subject analysis.

G. As the spreading flame passes over the thermocouple bead, the measured surface temperature rose to its maximum value and remained constant (see Fig. 7). It was found that, within the limits of data scatter (±25°C), this temperature is approximately 400°C and is independent of P, Y_{ox}, and inert diluent.

One conclusion is that direct surface attack by oxygen is unimportant during flame spreading. If it were, then changing the oxygen concentration by two orders of magnitude would have an important influence on the measured "ignition temperature." Thus, this finding represents additional evidence to support the author's assumption that the principal exothermic chemical reaction of significance in flame spreading takes place in the gas-phase. [Elsewhere in this volume workers from the University of Utah report a strong influence of surrounding environment on "ignition temperature"—but, in light of the present evidence, it is suggested that this apparent influence is a manifestation of their indirect way of arriving at the "ignition temperature," and their unrealistic assumption that thermal transport properties are temperature independent.]

During steady combustion of PMM with an impinging oxygen jet, the temperature at the vaporizing surface was found to be greater than

TABLE II

Experimental values of q and r for polymethylmethacrylate

Environmental composition	q	r
O_2/N_2	0	0.50
O_2/He	1.0	0.55
O_2/Ar	0.2	0.60

TABLE III

Calculated and experimental values of Φ and m for polymethylmethacrylate

		Environmental composition					
		O_2/N_2 ($s = 2.0$)*		O_2/He ($s = 2.3$)*		O_2/Ar ($s = 1.5$)*	
	β	Φ	m	Φ	m	Φ	m
Calculated	1.44	0.94	3.1	0.89	3.1**	0.84	2.4
Experimental		0.82	3.0	0.78	1.9	0.78	2.6

* Calculated from Eq. (19) of Ref. 13.

** Becomes 1.6 when suggested Lewis Number dependency is included.

500°C.[17] This large difference in surface-temperature level in the two cases suggests that caution should be exercised in extrapolating to unsteady combustion situations the surface-vaporization information obtained by steady-state experimentation.

To date the authors have found no evidence to refute the validity of the proposed continuous, diffusive, gas-phase-ignition theory of flame spreading. In addition to its success in predicting the flame-spreading characteristics of a wide variety of solid condensed-phase materials, recent experiments performed by the authors suggest that it will be equally successful for liquid fuels. [Caution must be exercised in separating the surface motion induced by the thermal expansion of the heated liquid beneath the flame from the apparent velocity in the laboratory coordinate system, in order to extract V.] Measured values of V for liquid fuels of low volatility—i.e., kerosene—are approximately equal to those reported herein for solid fuels.

It is believed that the flame-spreading process is sufficiently well understood that a rational basis for the engineering design of systems involving flame spreading is now possible. For example, as a consequence of the subject program, a rational basis for the selection of manned capsule environments has emerged for minimization of the rate of flame spreading following accidental ignition.[18]

ACKNOWLEDGMENTS

The authors thank J. A. Wrubel for obtaining the propellant flame spreading data.

This work was supported by NASA Grant NGR-31-003-014.

REFERENCES

1. Parker, K. H., Most, W. J., and Summerfield, M.: Astronaut. Acta *12*, 4 (1966).
2. Barrere, M. and Moutet, A.: Résultats Récents Obtenus sur les Systêmes Hybrides ou a Lithergols, Communication presented at XVII Congres International d'Astronautique, Madrid, 9–15 October 1966.
3. Vos, K., David, H., and Taylor, H.: Special Report: Apollo 204, Technology Week, Feb. 6, 1967.
4. Apollo Recovery, p. 97, Astronautics and Aeronautics, July 1967.
5. Emmons, H. W.: *Tenth Symposium (International) on Combustion,* The Combustion Institute, p. 951, 1965.
6. DeSoto, S. and Friedman, H. A.: Flame Spreading and Ignition Transients in Solid Grain Motors, AIAA Preprint 64–122, 1964; also AIAA J. *3*, 405 (1965).
7. Paul, B. E., Lovine, R. L., and Fong, L. Y.: Propellant Surface Flame Propagation in Rocket Motors, AIAA Preprint 64–125, 1964.
8. Mitchell, R. C. and Ryan, N. W.: Flame Spreading on Solid Propellant, AIAA Preprint 64–128, 1964; also J. Spacecraft Rockets *2*, 610 (1965).
9. Tarifa, S. C. and Torralbo, M. A.: *Eleventh Symposium (International) on Combustion,* p. 533, The Combustion Institute, 1967.
10. McAlevy, R. F. III, Magee, R. S., Wrubel, J. A., and Horowitz, F. A.: AIAA J. *5*, 2 (1967).
11. Friedman, R.: A Survey of Knowledge About Idealized Fire Spread Over Surfaces. Paper presented at 1967 Meeting of Eastern State Section, The Combustion Institute, Pittsburgh, Penna., Nov. 27–28.

12. McAlevy, R. F. III and Magee, R. S.: Flame Spreading at Elevated Pressures Over the Surface of Igniting Solid Propellants and Propellant Ingredients in Oxygen/Inert Environments, Annual Report (NASA Grant NGR–31–003–014, ME–RT 67011), Stevens Institute of Technology, Hoboken, N. J., October 1967.
13. Magee, R. S.: The Mechanism of Flame Spreading Over the Surface of Igniting Condensed Phase Materials, D.Sc. thesis, Stevens Institute of Technology, Hoboken, N. J., June 1968.
14. Hermance, C. E., Shinnar, R., and Summerfield, M.: Astronaut. Acta *12*, 95 (1966).
15. McAlevy, R. F. III, Wrubel, J. A., and Magee, R. S.: Flame Spreading Over The Surface of Double Base Propellants at High Pressure, Annual Report (NASA Grant NGR 31–003–014, ME–RT 66010), Stevens Institute of Technology, Hoboken, N. J. October 1966, p. 17.
16. McAlevy, R. F., III, Cowan, P. L., and Summerfield, M.: The Mechanism of Ignition of Composite Solid Propellants by Hot Gases, in Progress in Astronautics and Rocketry: Solid Propellant Rocket Research, Vol. 1, p. 652, Academic Press, 1960.
17. McAlevy, R. F. III, Lee, S. Y., and Smith, W. H.: AIAA J. *6*, 1137 (1968).
18. McAlevy, R. F. III and Magee, R. S.: J. Spacecraft Rockets *4*, 10 (1967).

COMMENTS

H. W. Emmons, Harvard University. The authors present some excellent flame-velocity data that shows an unusually excellent correlation with gas-phase parameters. Before we can conclude that the spread rate is controlled by the gas phase only, we must know whether the solid-phase parameters varied in the different tests. Can the authors supply any information on the variation of such solid-phase parameters as thermal conductivity, thermal diffusivity, pyrolysis temperature, heat of pyrolysis, etc.

R. F. McAlevy and R. S. Magee. The flame spreading phenomenon involves a complex chain of interconnected processes, so it might be unrealistic to think of one as having a rate that "controls" the rate at which the over-all phenomenon itself proceeds. Nevertheless, some thought has been given to testing the influence of solid-phase parameters on flame-spreading velocity. For example, in the authors' view, the solid-surface *transient* vaporization characteristics (which might be described in terms of pyrolysis temperature, heat of pyrolysis, etc.) are pivotally important, but they are currently unknown for all materials. And so there is no hope at the present of a meaningful investigation of the influence of this factor on the flame-spreading velocity. Further, with the exception of ammonium perchlorate, all the materials tested have transport parameters (thermal conductivity and thermal diffusivity) that lie within a factor of 3 (which is probably true for most organic solids of interest), and there was no apparent correlation of flame-spreading velocity with these parameters. But, even assuming that the factor-of-5 difference in flame-spreading rates of the thermoplastics and nitrate ester propellants is due not to chemistry, which it probably is, but rather to some "solid-phase parameters," the flame-spreading rate of each can be changed by a factor of 100 by changes of gas-phase parameters. It is this powerful effect that suggests that, in the chain of processes involved in flame spreading, the gas-phase link is of paramount importance, although the authors realize that no link can be neglected if the phenomenon is to be understood completely.

M. Barrere, ONERA. Your experiments show that the influence of pressure on flame-spreading velocity seems to be well defined and measurable, whereas it is much less so in ignition experiments and depends upon the experimental apparatus. There is even a wide scatter in the results from one author to the other. It is therefore most important to measure ignition delays and flame-spreading velocities in the same experiment, at least so long as ignition phenomena are not better known.

R. F. McAlevy and R. S. Magee. Barrere's observation that flame-spreading data are more reproducible than ignition data is correct and can be rationalized in the following way.

The two most probable sources of data scatter in solid-propellant ignition experiments are: (1) differences in actual surface heating exposures, and (2) differences in criteria for determining the instant of ignition. During flame spreading, the surface heating exposure is provided by the advancing flame itself, rather than by an externally imposed stimulus, which eliminates (1), and instead of working with the ignition-criterion-dependent ignition delay, the intrinsically related flame-spreading velocity is obtained, from the generally well-defined position of the flame front, which eliminates (2).

The connection between ignition delay and flame-spreading velocity developed in our paper could be employed to extract very useful ignition-delay information from flame-spreading data.

◆

Perry L. Blackshear, University of Minnesota. In the event the flame-spread rate is much slower than the normal laminar flame speed, I would expect the heat flux to the surface to be related to the size of the fuel bed (i.e., the way steady-state burning rates of fuel slabs vary with size). We have found that as the size increases, heat flux first decreases, remains constant, then increases sharply, and finally reaches a plateau at sizes of approximatively 1 meter. For the larger flames, radiation heat flux is perhaps 5 times that of convective flux and has a range of influence on the order of flame diameter.

Jack B. Howard, Massachusetts Institute of Technology. Your conclusion that radiation is important in flame propagation along such small specimens as those employed in your experiments is very interesting, especially since some rather low pressures were employed. Would you point out the experimental basis of this conclusion? Does the observed influence of pressure on flame-propagation velocity agree with predictions based upon radiative energy transport?

R. F. McAlevy and R. S. Magee. The senior author mentioned during presentation of the paper that radiation from the flame to the solid surface lying before it appeared to be the principal mode of heat transfer forward. As the supporting evidence was incomplete, no mention of this was made in the paper itself. But in response to Prof. Howard's question, a bit of the evidence will be presented here.

It was observed that when propellant B was tested in air at atmospheric pressure, the flame-spreading velocity increased by 25% when the width of the specimen was increased from 0.375 in. to 0.75 in. Calculations show that the "view factor" for radiant heat transfer from the flame to the propellant surface lying a distance δ ahead of the flame also increased by about the same amount, and therefore, so did the radiant-flux level. Thus, in this very limited range of experimentation, it appears that flame-spreading velocity is linearly dependent on radiation-flux level. But, much more data need be taken before a general conclusion can be drawn. Until this information is available it seems premature to work out a detailed scheme for predicting the pressure effect on radiative energy transport.

◆

G. S. Pearson, Rocket Propulsion Establishment, Westcott. Can you relate these results on flame spread over fuels in oxygen to flame spread over a composite propellant containing ammonium perchlorate in an inert atmosphere? Would the mechanism change under these conditions?

R. F. McAlevy and R. S. Magee. Flame spreading over the surface of condensed-phase materials is postulated to be a process of continuous, diffusive, gas-phase ignition. To date, we have treated analytically the case of a single-component solid material (either fuel or oxidizer) in a gaseous environment containing a component with which it can react chemically. However, the postulated mechanism of flame spreading is believed to be valid also when both reactive components are initially in the solid phase. Of course, in this case, both components must vaporize and inter-diffuse before ignition, and hence flame spreading, can occur. For composite solid propellants, the *transient* diffusion process is three dimensional in nature, and therefore analytical treatment will be much more difficult than the case treated in the paper. (To put into perspective the complexity of this problem, the reader is reminded that the composite-solid-propellant deflagration mechanism is essentially unknown in detail, principally because the underlying *quasi-steady,* three-dimensional diffusion process could not be treated successfully.) Nevertheless, a study of the composite-propellant flame-spreading mechanism is currently under way in the authors' laboratory.

N71-31430

PART IV

FLAME SPREADING OVER THE SURFACE OF IGNITING SOLID ROCKET PROPELLANTS AND PROPELLANT INGREDIENTS

VOL. 5, NO. 2, FEBRUARY 1967 AIAA JOURNAL 265

Flame Spreading over the Surface of Igniting Solid Rocket Propellants and Propellant Ingredients

ROBERT F. McALEVY III,* RICHARD S. MAGEE,† JOHN A. WRUBEL,‡ AND FRED A. HOROWITZ§
Stevens Institute of Technology, Hoboken, N. J.

The velocity at which a flame spreads over the surface of igniting nitrate ester propellants, ammonium perchlorate, and thermoplastics has been measured as a function of pressure level and chemical nature of the surrounding, quiescent atmosphere, as well as specimen surface condition. Small test specimens, mounted horizontally, prepared surface upward, in a relatively large test chamber, were ignited and the flame-spreading velocity cinematographically obtained. Flame-spreading velocity was found to vary: directly with pressure level (between 0.1 and 1.0 atm); directly with oxygen fraction of environments composed of oxygen-nitrogen mixtures; and inversely with specimen surface smoothness. For rough-surfaced specimens, photographic evidence of random ignition sites ahead of the spreading flame has been obtained, presumably a result of enhanced radiant heating. A gas-phase model of flame spreading is presented; flame spreading is viewed as a continuous gas-phase ignition process. For smooth-surfaced specimens, an analytical prediction of flame-spreading velocity dependence on gas-phase parameters is supported by the data obtained.

Introduction

THE rapidly expanding utilization of solid propellant propulsion systems during the past decade or so has given rise to a rather large number of solid propellant rocket motor ignition studies. Historically, the treatment of motor ignition has been a purely empirical matter, and to a great extent it remains so even today, despite this recent flourish of attention. It is hoped, perhaps optimistically, that as a result of these studies it will be possible to establish a valid basis for the rational design of ignition systems, or at least to evolve a set of rules for the scaling of successful systems to meet the requirements of new applications. Ideally, it should become possible to calculate the minimum weight of igniter charge that is perfectly matched to any motor, in order to produce an optimized ignition pressure transient, without excessive pressure rise or ignition delay, but which is highly reliable over a wide range of operating conditions.

Almost every type of operational igniter acts by heating exposed surfaces of the propellant grain—the source of energy being the hot products produced by combustion of the igniter material. The over-all motor ignition process, following igniter firing, can be thought of most conveniently as being comprised of three principal phases: 1) heating of the exposed grain surface to incipient ignition conditions, and the actual development of ignition at some locations; 2) spreading of the flame over the remainder of the surface; and finally 3) filling the chamber with propellant combustion products until the equilibrium chamber pressure level is reached. In many systems the igniter continues to fire during the flame-spreading and chamber-filling phases, thus necessitating that its influence be accounted for in any completely valid description of these systems.

A great variety of heating inputs are possible, depending on the type of igniter employed. For example, the propellant surface might be exposed to a complex combination of conduction, convection, and radiation heating, heat liberated by condensation of certain vapors, heating due to exothermic chemical reactions with hypergolic igniter components, etc. Several elementary experiments have been designed to measure propellant ignition response to one or more of these ignition stimuli. A number of techniques have been employed in this regard—electrically heated wires,[1] detonation tubes,[2] shock tubes,[3,4] arc-imaging furnaces,[5] exposure to powerful oxidizing agents,[6] and many others.[7,8] These have demonstrated that, in general, propellant ignition delay varies inversely with surface heating rate, pressure level, and chemical reactivity of the surrounding atmosphere. Current interpretations of these results are divided into two schools: that which considers the principal exothermic processes leading to ignition to take place in the gas phase following some vaporization of propellant constituents; and that which considers the principal exothermic processes to take place on the solid propellant surface, leading to vaporization. However, even in this latter interpretation, it is necessary to account for the subsequent gas-phase exothermic processes in order to arrive at a complete description of the ignition event.

Recent experiments in this laboratory,[9,10] as well as those in others,[22] have led the present authors to conclude that whereas it is probable that thermochemical attack on a propellant surface by a certain class of violent oxidizing agents, e.g., F_2 and ClF_3, could lead to ignition via a heterogeneous reaction, it is highly unlikely that this mechanism is valid when less powerful agents, such as O_2, are present. Thus it is believed that, when violent oxidizing agents are not present, propellant ignition, both in the laboratory and in rocket motors, is principally a gas-phase process. Following flame spreading over the entire surface, the pressure rise to the equilibrium chamber pressure level can be described quite simply—it is obtained from a balance between the rate at which gas is being generated, both by igniter combustion and combustion of the propellant grain, and the rate at which it is being expelled through the nozzle, while suitably accounting for thermal energy generation and exchange.[23]

The phase of motor ignition that has received the least attention is that of the flame spreading from areas of first ignition to eventual coverage of the entire grain surface. During the successful ignition of small motors this phase is completed within a few milliseconds. The enormous grain surface area of massive space booster motors sometimes results in a protraction of this interval to about one second, and therefore it

---

Presented as Preprint 66-68 at the AIAA 3rd Aerospace Sciences Meeting, New York, January 24–26, 1966; submitted January 28, 1966; revision received September 7, 1966. This work was supported by NASA Grant NGR-31-003-014.

* Professor and Director of the Combustion Laboratory. Associate Fellow AIAA.

† Graduate Student, currently Assistant Research Engineer, Department of Mechanical Engineering.

‡ Graduate Student, Department of Mechanical Engineering; currently Senior Engineer, Rocketdyne Division, North American Aviation, Canoga Park, Calif.

§ Graduate Student, Department of Mechanical Engineering.

Reprinted from AIAA JOURNAL

becomes an item of considerable interest when precise firing schedules must be met, e.g., when these motors are "clustered." Finally, it appears as if the time for flame spreading might be the most difficult to reduce in the development of antimissile missile boosters, where promptness in achieving full motor ignition is at a premium.

It has not been possible to establish a thoroughgoing, fundamental understanding of the phenomenon of flame spreading over an igniting solid propellant surface. A number of preliminary studies have been reported.[11-15,23] However, all but one of these focused on the flame-spreading phenomenon in situations that were sufficiently complex—principally because of the presence of strong forced convection—to preclude elucidation of the underlying mechanism. That one[15] was based on an elementary laboratory experiment designed to measure the response of flame-spreading velocity to variation of environmental conditions. It bears the same relationship to the second phase of motor ignition that the elementary ignition experiments[1-8] bear to the first phase and, now completed, is described herein.

Composite solid propellants are composed of a heterogeneous mixture of ingredients. Recently, it has been recognized that an excellent way to arrive at an understanding of the combustion phenomena of these propellants is to start by investigating the behavior of the individual ingredients separately. This approach has been employed previously in studies of the ignition phenomenon[4] and the deflagration phenomenon,[16] and has been taken for the subject study of the flame-spreading phenomenon. The flame-spreading velocity over the surface of two thermoplastics, typical of composite propellant fuel-binders as well as the fuel component of hybrid rocket motors, was measured in mixtures of oxygen and nitrogen. The flame-spreading rate over the surface of ammonium perchlorate, currently the most popular composite propellant oxidant, was measured in methane. Mixtures of ammonium perchlorate crystals and polystyrene beads were also tested. Specimen surface condition was varied widely and employed as an independent test parameter. Nitrate ester (double-base) propellants were tested so that the flame-spreading characteristics of this homogeneous type of propellant could be compared with those of the heterogeneous type. The dependence of flame-spreading velocity on double-base propellant chemical energy level was investigated, as the three propellants selected differed principally in nitroglycerine-nitrocellulose ratio.

Theory

The phenomenon of flame spreading over an igniting propellant surface is viewed herein as one of continuous ignition; thus, the flame-spreading phenomenon is linked inextricably to the ignition phenomenon. When a flame spreads smoothly over an igniting propellant, the elements of surface lying before it are brought successively to ignition by the influence of the approaching flame—the propellant element immediately ahead of it being at a condition of incipient ignition and ignition delay of the elements increasing monotonically with increasing distance from the flame. [Note: Surface roughness could intensify radiant heat flux at certain locations, thus reducing ignition delay and producing early ignition at sites relatively far ahead of the flame. The resulting nonsmooth flame-spreading process lies within the compass of the model proposed, but not of the analysis presented.]

The conclusion of others[8] surveying current understanding of the solid propellant ignition phenomenon, as well as recent experimental results,[9,10,22] has led the authors to believe that the principal exothermic process leading to solid propellant ignition takes place in the gas phase following some vaporization of propellant constituents. In the rare event when violent oxidizing agents, such as F_2 and ClF_3, are present at the igniting propellant surface, the heating generated by direct surface attack probably has a strong influence on ignition and flame spreading. However, this exotic process was not studied during the subject program and is not included in the model proposed herein.

The elucidation of the gas-phase mechanism of solid propellant ignition was evolved from conductive heating experiments,[4] and the first analytically predicted dependence of ignition delay time on exposure condition resulted from a "zeroth-" order solution to an approximate form of the energy equation, which had been uncoupled from the remaining conservation equations.[4] A few year's work and an electronic computing machine were required to obtain solutions to the complete set of conservation equations,[17] and only now is the gas-phase mechanism of solid propellant ignition being investigated analytically for convective heating.[18] In the present scheme of things, the subject effort in elucidating the flame-spreading mechanism is on a level analogous to the ignition work described in Ref. 4. However, theoretical analysis of the flame-spreading phenomenon is materially more difficult. It involves heat flux forward from a moving flame at a right angle to the flux of propellant vapors up from the surface, whereas in the analogous ignition situation[4] the heat flux is from a still gas environment and the propellant vapor flux is in parallel with it. Therefore it should be expected that this first analysis of the gas-phase flame-spreading mechanism will be on an even more primitive level than that first analysis of the gas-phase ignition mechanism.

The assumptions underlying the analysis, in addition to that of smooth flame propagation, are:

1) The distance ahead of the approaching flame (thermal-layer thickness) which is affected by the presence of the flame is constant.

2) The principal exothermic processes leading to ignition takes place in the gas phase; it results in a temperature "runaway" at a distance above the surface, X^*, which is taken to be constant.

3) The concentration of test gas at X^* is unaffected by the diffusing propellant vapor.

4) The propellant vapor concentration at X^*, $(C)_{x^*}$, is proportional to ρt^n, where ρ is the gas density, t is the time following the instant when the flame presence is first felt, and n is a positive constant (see Ref. 19 for exact solutions to controlling mass diffusion equation).

5) The chemical reaction between propellant vapors and test gas—the only reaction considered in this analysis—is second order.

6) The rate of heat loss or gain from the ignition location is negligible compared with the rate of chemical heat production at that site.

7) The temperature dependence of chemical reaction rate follows the Arrhenius expression, and the high value of activation energy for the controlling kinetics justifies the use of a gas-phase "ignition temperature" concept.

At the site of ignition, the energy equation takes the form

$$\rho C_p\, dT/dt = \dot{Q}_{\text{chem}} \tag{1}$$

where

ρ = the density (mass/unit volume)
C_p = the heat capacity/unit mass
T = the absolute temperature
t = time
$\dot{Q}_{\text{chem}}$ = the rate of chemical heat production

Within the framework of the assumptions

$$\dot{Q}_{\text{chem}} = q(C)_{x^*}C_gAe^{-E/RT} \tag{2}$$

where

q = the heat of combustion of the gas-phase reactants/unit mass
C_g = the concentration of the reactive component in the test gas (mass/unit volume)

A = the Arrhenius pre-exponential factor [(mass/unit volume)$^{-1}$/unit time]
E = the activation energy for the gas-phase reaction
R = the universal gas constant

Substituting $(C)_{x*} \propto \rho t^n$ in (2) yields,

$$Q_{\text{chem}} \propto q(\rho t^n) C_g A e^{-E/RT} \tag{3}$$

and noting that $C_g = Z\rho$, where Z is the weight fraction of the chemically reactive component in the test gas, Eq. (1) becomes

$$\rho C_p dT/dt \propto q\rho^2 Z t^n A e^{-E/RT} \tag{4}$$

Assuming perfect gas behavior, $\rho = p/RT$, where P is the pressure in the surrounding atmosphere, (4) can be written as

$$\left[\frac{RC_pT}{qAe^{-E/RT}}\right]\frac{dT}{dt} \propto ZPt^n \tag{5}$$

All terms within the brackets are constants of the system, except T, so that it can be represented as a function of T only, say $f(T)$. Thus, this takes the form

$$f(T)dT \propto ZPt^n dt \tag{6}$$

When integrated between the limits: $t = 0$ when $T = T_0$, where T_0 is the initial temperature; and $t = \tau$ (where τ is the ignition time delay) when $T = T_{\text{ig}}$, where T_{ig} is the "ignition temperature," (6) becomes

$$\int_{T=T_0}^{T=T_{\text{ig}}} f(T)dt \propto ZP\tau^{n+1} \tag{7}$$

Assuming both T_0 and T_{ig} constant, (7) becomes

$$\tau \propto (ZP)^{-1/(n+1)} \tag{8}$$

Now, remembering that 1) τ is the interval between the instant at which the advancing flame first produces a significant effect at a certain location and the instant at which ignition of the propellant vapors occurs at that location, and 2) that the distance ahead of the flame that is affected by the presence of the flame is assumed to be a constant, then the flame spreading velocity V must vary inversely with τ. That is,

$$V \propto 1/\tau \propto (ZP)^{1/(n+1)} \tag{9}$$

Thus, this simplified analysis predicts a power law dependence of V on Z and P, with an exponent, $m \equiv 1/(n+1)$, having a value less than unity, as n must always be positive.

Experimental Approach

Small test specimens, mounted horizontally, freshly prepared surface upward, in a relatively large vacuum-tight test chamber ($8\frac{1}{2}$-in. i.d. × 18 in.) were ignited by an electrically heated wire placed along the top edge, and the flame spreading was recorded by means of a motion picture camera. This approach completely eliminated complications of the flame-spreading process due to forced convection; and virtually eliminated the complication of the free convection effects, immutably linked to the spreading ignition wave itself, that nearby objects would produce. Pressure increase of the surrounding atmosphere during flame spreading was rendered negligible by connecting to the test chamber a large tank (10 ft^3). An unobstructed view of the phenomenon within the chamber was provided by an observation window, through which the event was filmed (Fig. 1).

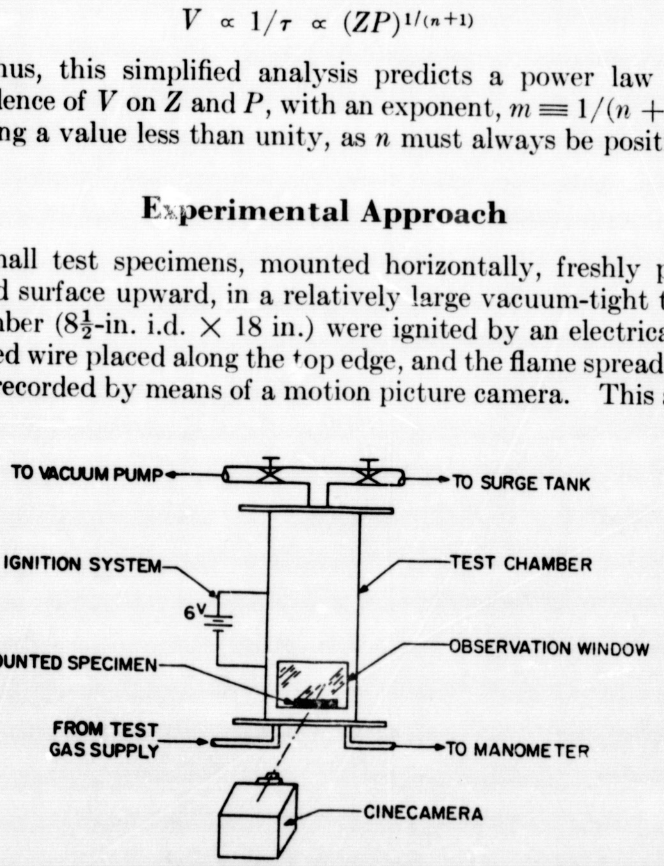


Fig. 1 Schematic of apparatus for flame spreading velocity measurement.

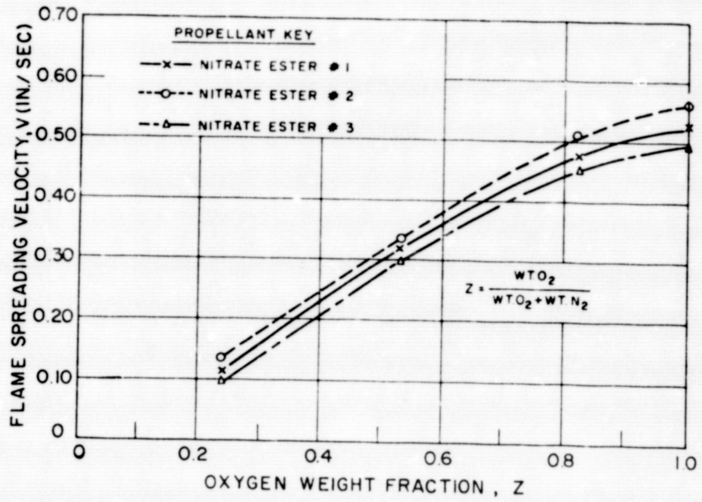


Fig. 2 Influence of Z on V at atmospheric pressure for three nitrate ester propellants.

In order to insure uniform and simultaneous ignition across the short side of the top edge of the specimen surface, it was necessary to fasten the ignition wire tightly to the surface. In order to prevent a too rapid spreading of the flame along the long edge of the specimen—a phenomenon that takes place faster than flame spreading over the surface, and therefore could result in spuriously higher measured values for the latter process—it was necessary to inhibit the edges of most specimens. An inorganic cement, consisting of asbestos and water glass in a weight ratio of 1:5 and applied to the sides of these specimens, produced, when dried, a firmly bonded protective coating. Further development demonstrated that the effectiveness of this inhibition could be improved by extending the side coating over the edge and onto the top for a distance of about $\frac{1}{32}$ in. This technique was employed to inhibit all specimens requiring it. After mounting a specimen in the chamber and sealing, it was evacuated and charged with the selected test gas. Evacuation and charging was repeated twice more to insure that the gas in contact with the specimen would be, in fact, the selected test gas. Finally, the pressure in the chamber was brought to the desired level and the specimen ignited.

The event was recorded on motion picture film, exposed at a calibrated rate of 48 frames/sec, and, following development, a motion analyzer was employed to obtain the flame-spreading velocity, i.e., the measured propagation distance per 24 (or, in some cases, 48) frame intervals. It was noticed that immediately following ignition, the spreading velocity was somewhat unsteady, although it became steady well before the flame had spread to the specimen midpoint. Nevertheless, only spreading over the final half of each specimen was analyzed and reported herein.

Results and Conclusions

Nitrate Ester Propellants

Three types of nitrate ester propellants, obtained through the kindness of J. P. Picard, R. G. Wetton, and R. F. Jasinski of the Propellant Laboratory, Feltman Research Laboratory Division, Picatinny Arsenal, Dover, N. J., were subjected to test. They are designated here as propellants 1, 2, and 3, in order of ascending nitroglycerine-to-nitrocellulose ratio con-

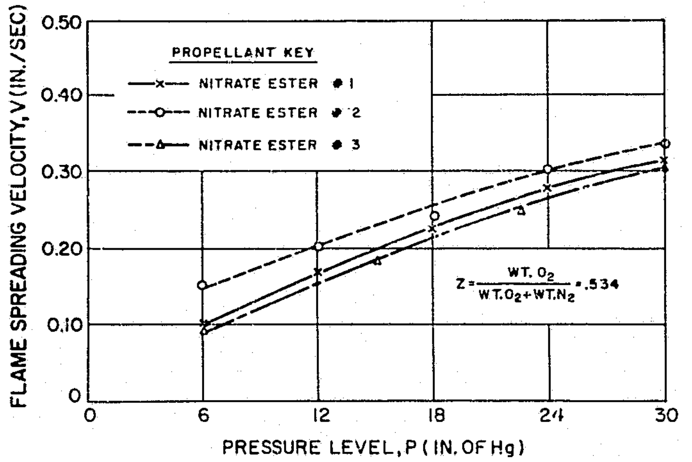


Fig. 3 Influence of P on V in Z = 0.534 test gas for three nitrate ester propellants.

tained by each. (The exact compositions cannot be revealed here.)

The specimen surface ($1\frac{1}{2} \times \frac{3}{8}$ in.) was cut and polished to a smooth finish, and then the sides and about a $\frac{1}{32}$-in. perimeter of the prepared surface were inhibited. The flame-spreading velocity in the $1\frac{1}{2}$-in. direction was measured: at atmospheric pressure for 4 different mixtures of oxygen and nitrogen (Fig. 2); in a $Z = 0.534$ mixture of oxygen and nitrogen at 4 subatmospheric pressures (Fig. 3); and in oxygen ($Z = 1$) at 4 subatmospheric pressures (Fig. 4). The spreading flame was in all cases well defined, propagated uniformly after being established, and remained perpendicular to the long side of the specimen. With the exception of one testing condition, all data obtained were within $\pm 6\%$ of the best fit curve drawn through the arithmetic mean points, and most were within $\pm 3\%$.

The analysis presented herein predicts, from Eq. (9),

$$V \propto (ZP)^m$$

where m is a constant having a value less than 1. When the data depicted in Figs. 2–4 are plotted as log V vs either log Z or log P, a small (15%) decrease of m, from a value close to 1, is exhibited as the independent variable increases. The lowest values of the independent variables at which reproducible data were obtained are very close to the lower limit of flame spreading for the propellants tested. Since the lower limit of combustion wave propagation is probably a result of quenching because of excessive heat loss,[20] the present analysis should misrepresent the flame-spreading phenomenon near the limiting conditions as it is based on the assumption of an adiabatic ignition site. By employing as a reference condition (p_R and Z_R) the point of lowest reproducible flame-spreading velocity (V_R) in Figs. 2–4, Figs. 5–7 were plotted.

From Fig. 5 it can be seen that the slope ≈ 0.9 for propellant 2 and decreases with increasing Z for propellants 1 and 3. (Unfortunately, it was necessary to select as reference a condition that produced more than double the average data scatter, and therefore probably was too near the limiting conditions. It would have been extremely difficult to obtain additional propellants; consequently, it was not possible to establish a more meaningful reference condition and Fig. 5 must stand as it is.) Although the indicated slopes are less than unity, they are not constant. But no conclusions concerning the theory's validity can be drawn on the basis of these data because of the questionable selection of the reference condition. All the data in Figs. 6 and 7 exhibit fractional exponents over the range of pressures tested, and they are essentially independent of chemical reactivity level in the surrounding atmosphere. This is strong support for the theory.

The sensitive dependence of V on both Z and P exhibited by the propellants is quite striking and calls to mind the previously observed inverse dependence of ignition delay on these parameters, reported in Ref. 21. Indeed, comparison of the results from these different experiments suggests a very strong link between the two processes. For example, the propellant (#3) that took longest to ignite also took longest to spread a flame, whereas the propellant that was quickest to ignite (#2) exhibited the most rapid velocity of flame spreading. This is taken as additional support for the capital assumption of the model presented: that the basic mechanism of flame spreading is one of continuous ignition in the gas phase. Finally, it is noted that flame-spreading characteristics (or ignition characteristics) cannot be correlated with propellant nitrocellulose-to-nitroglycerine ratio, an index of heating value or chemical heat release.

Ammonium Perchlorate

Ammonium perchlorate crystals (99.7% pure, rounded crystals, American Potash and Chemical Corporation, Los Angeles, Calif.) between 297 and 500μ in diameter were subjected to test. The crystals were poured into a $1\frac{1}{2}$-in.-long $\times$ $\frac{1}{2}$-in.-wide $\times$ $\frac{3}{8}$-in-deep slot milled into aluminum stock, and lightly pressed to form a level surface. By leaving a small space between the top of the specimen and the top of the slot, it was possible to eliminate the edge effect without inhibition.

Another type of ammonium perchlorate test specimen was fabricated by hydraulically pressing the crystals in a hardened steel mold at pressures up to 16,000 psi for ten minutes (in order to relieve internal stresses). The ($3 \times \frac{3}{8}$ in.) specimen test surface became smoother as the hydraulic pressure was increased. It was necessary to inhibit the $\frac{1}{2}$-in. sides and a small perimeter of the test surface in order to eliminate the edge effect. All ammonium perchlorate specimens were tested in methane at various subatmospheric pressures.

The spreading flame was in all cases well-defined, propagated uniformly after being established, and remained perpendicular to the long side of the specimen. All data ob-

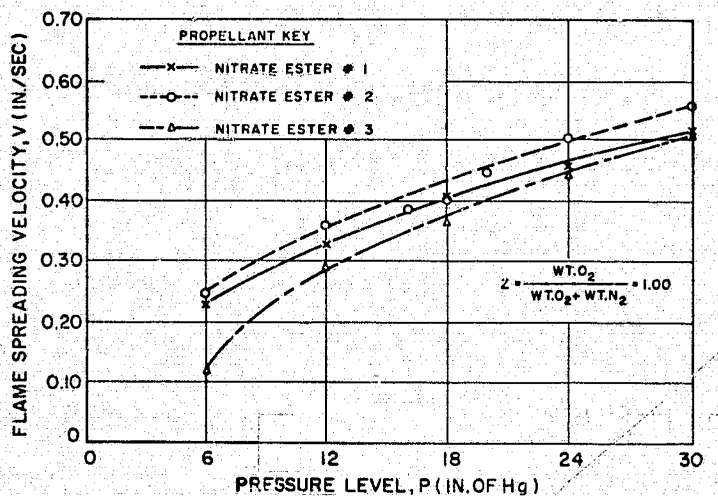


Fig. 4 Influence of P on V in Z = 1.00 test gas for three nitrate ester propellants.

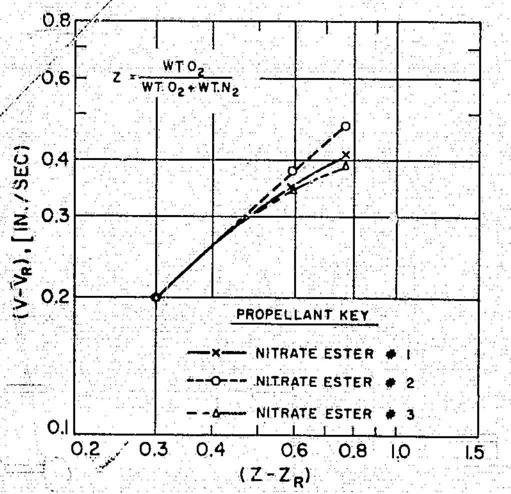


Fig. 5 Log-log plot of (V-V_R) at atmospheric pressure for three nitrate ester propellants.

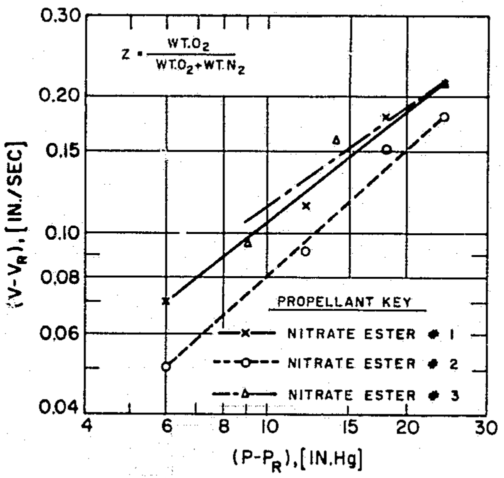


Fig. 6 **Log-log plot of (V-V_R) vs (P-P_R) at Z = 0.534 for three nitrate ester propellants.**

tained were within ±4% of the best fit curves drawn through arithmetic mean points. The dependence of flame-spreading velocity on pressure level is displayed in Fig. . By employing as reference condition the point of lowest reproducible flame spreading velocity, Fig. 9 was plotted.

The flame-spreading velocity is accelerated by the rough surface of the loose beads. Both types of specimens display a power law dependence of V on P, with the value of the exponent dependent on surface condition but independent of pressure level. Visual inspection of the pressed strand surfaces revealed that surface roughness decreased with increasing pressure of compaction. Unfortunately, the available press was limited to 16,000 psi operating pressure and the strand surface produced at this level was still noticeably rough (about 10% of the surface area contained holes approximately the size of a crystal). Thus, it was impossible to determine if the pressure exponent for ammonium perchlorate would fall significantly below unity for a sufficiently smooth surface, i.e., a surface produced by press pressures greater than 16,000 psi. The acceleration of V with surface roughness suggests that a substantial fraction of the heat transfer from the spreading flame to the surface ahead is by radiation. Local intensification of surface heat flux results when local surface roughness increases the "view factor" for radiation heat transfer—by turning area elements to face more directly the impinging radiation. This will result in a net increase of heat-transfer rate forward, and therefore a net acceleration of V.

The analysis presented herein is based on an assumption that the ignition delay of surface elements ahead of the spreading flame decreases monotonically to zero as the distance to the flame zone is decreased. The surface-roughness-induced local intensification of heat flux, which presumably produces a local acceleration of surface vaporization rate, is responsible for a local decrease in ignition delay at random sites ahead of the spreading flame. (Photographic evidence in support of this is presented below.) The random variation of ignition delay with distance ahead of the flame is a direct violation of the assumed monotonic variation, and therefore the results of the analysis are not applicable in this case. Nevertheless, it is believed that flame spreading over the surface of igniting ammonium perchlorate does take place by means of a gas-phase ignition process, as V depends strongly on the state of the gas phase.

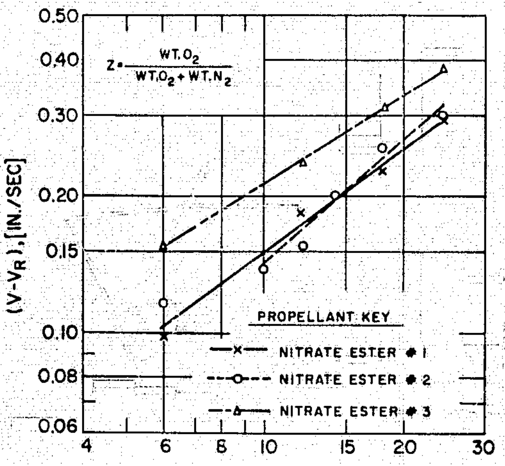


Fig. 7 **Log-log plot of (V-V_R) vs (P-P_R) at Z = 1.00 for three nitrate ester propellants.**

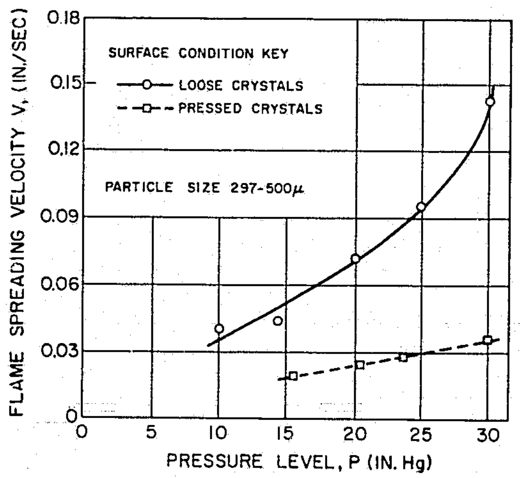


Fig. 8 **Effect of pressure level on flame spreading velocity for ammonium perchlorate samples in 100% methane as a function of surface condition.**

Polystyrene

Spherical polystyrene pellets (Dylene 8X, Koppers Company, Plastics Division, Manaca, Pa.), 350–420 μ in diameter, were subjected to test. Loose pellets were poured into a 1½-in.-long × ½-in.-wide × ⅜-in.-deep slot milled into aluminum stock, and lightly pressed to form a level surface. By leaving a small space between the top of the specimen and the top of the slot, it was possible to eliminate the edge effect without inhibition. Some specimens were prepared by exposing the beads to a methylethylketone-water solution to produce, when dried, a chemically bonded surface that was much smoother than the loose bead surface, but still retained some surface roughness; these required no inhibition. Other specimens were prepared by pressing to 16,000 psi, in the mold employed to fabricate ammonium perchlorate strands; because of the resiliency of this material, the surface condition resembled that of the loose beads, except that the tops of the individual spherical beads were flattened to about half their original height; these required inhibition. In addition,

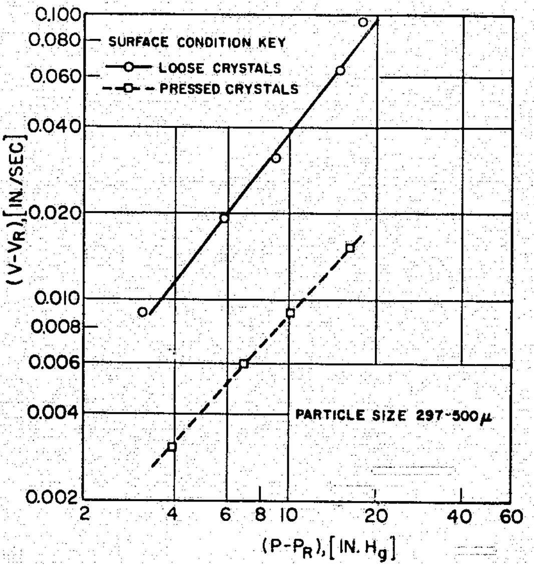


Fig. 9 **Log-log plot of (V-V_R) vs (P-P_R) for ammonium perchlorate samples in 100% methane as a function of surface condition.**

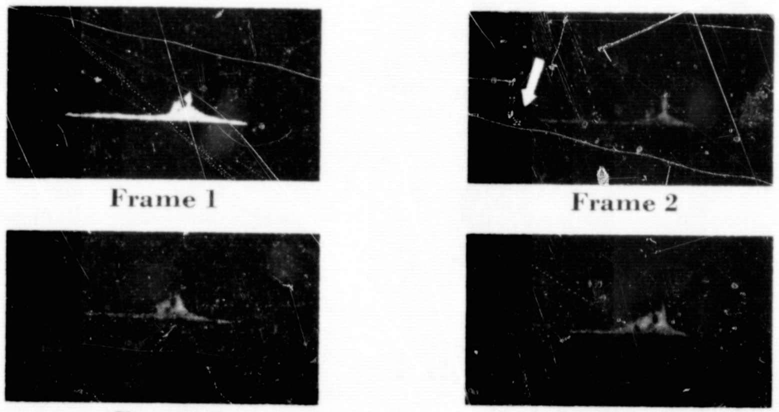

Frame 1
Frame 2
Frame 5
Frame 10

Fig. 10 Stages of flame spreading over a surface of polystyrene beads.

solid polystyrene (polished, high impact, Almac Plastics Incorporated, Newark, N. J.) was prepared; it was necessary to inhibit the $\frac{1}{2}$-in.-high sides as well as a $\frac{1}{32}$-in. perimeter of the ($1\frac{1}{2}$- × $\frac{3}{8}$-in.) test surface. All specimens were tested in oxygen at various subatmospheric pressures.

The spreading flame was well defined for all specimens except for the loosely packed beads, where random ignition sites ahead of the spreading flame were noticed. This flame appeared to "jump" forward to ignite particles lying ahead of the principal flame, thus producing flame discontinuities along the sample. Photographic evidence of this phenomenon is presented in Fig. 10. These frames show flame spreading over polystyrene beads in oxygen at atmospheric pressure, and were taken at a rate of 48 frames/sec. Frame 2 shows an incipient flame ahead of the main flame (arrow); frame 5 shows it spreading back towards the approaching main flame; and frame 10 shows it merged with the main flame. Figure 11 shows the dependence of polystyrene flame-spreading velocity on pressure level for all types of specimens. With the exception of the loose beads, all data obtained were within ±3% of the best fit curve drawn through the arithmetic mean points, and were otherwise well behaved. The unsteadiness of the loose bead surface flame spreading process resulted in a maximum data scatter of ±6%. Figure 12 shows that only the solid polystyrene exhibited a pressure exponent less than unity, as predicted by the analysis presented herein. The exponents for the others were all greater than unity, indicating that the ignition delay for these specimens did not vary monotonically with distance from the flame front (Fig. 10).

Polymethylmethacrylate

Polymethylmethacrylate pellets were ground from molding power (Type VS-100 Plexiglas, Rohm and Hass Company, Philadelphia, Pa.) to a size between 350 and 420μ, and specimens prepared in the same manner as with the polystyrene beads. Also, solid polymethylmethacrylate (polished, Plexiglas II UVA, Almac Plastic Incorporated, Newark, N. J.) was prepared in the same way as the solid polystyrene. For all conditions tested, the polymethylmethacrylate flame-spreading rate was about 15% below the corresponding polystyrene rate. (In order to save space, these data will not be displayed.) The solid polymethylmethacrylate data support the analysis presented herein (slope ≈0.6), whereas the rough surface of the loose bead specimen produces a condition (ignition ahead of the main flame) that precludes comparison of the resulting flame-spreading data to prediction.

The structure of the spreading polymethylmethacrylate (PMM) flame is quite different from that of the polystyrene (PS) flame (Fig. 13). In Fig. 13, the flame spreads from right to left. Besides being less bushy, the leading edge of the PS flame is light blue in color. The PMM flame exhibits no blue at the leading edge. Previously,[16] it had been suggested that PS burns with a two-stage flame, the lighter fragments (H_2, CH_4, etc.) of pyrolysis burning near the surface and the larger fragments burning to completion in a later stage. The light blue leading edge suggests fuel lean combustion of light species, and therefore tends to confirm the two-stage model of PS combustion.

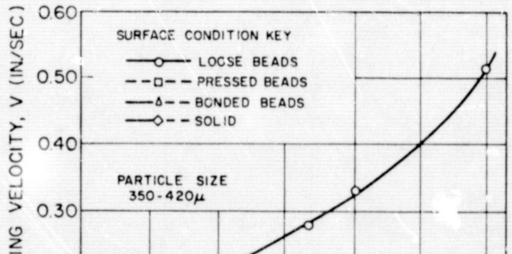


Fig. 11 Effect of pressure level on flame spreading velocity for polystyrene samples in 100% oxygen as a function of surface condition.

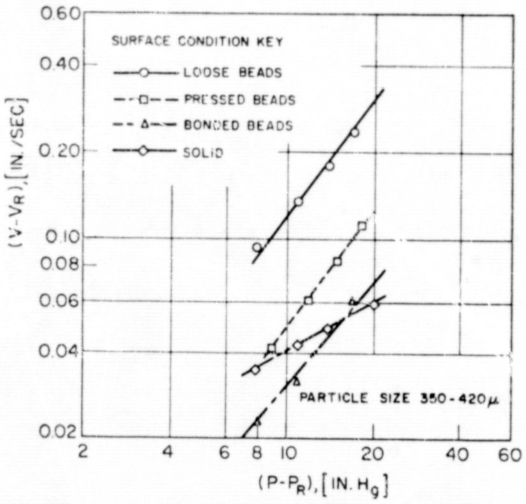


Fig. 12 Log-log plot of $(V-V_R)$ vs $(P-P_R)$ for polystyrene samples in 100% oxygen as a function of surface condition.

Ammonium Perchlorate—Polystyrene Mixtures

Mixtures of ammonium perchlorate (AP) crystals (297–500μ) and polystyrene (PS) beads (350–420μ) were prepared. Specimens were tested in oxygen in the same manner as the loose PS beads. Sustained flame spreading occurred only in the range of mixture ratios where steady deflagration of these mixtures has been recorded.[16] As previously experienced with rough surfaces, the flame moved forward somewhat unsteadily, igniting PS beads ahead of the main flame; the AP crystals ignited only after the polystyrene-oxygen flame had passed over them. (This early ignition of fuel-binder followed by later ignition of the ammonium perchlorate has been observed[4] with composite solid propellant ignition as well.)

In the interest of saving space, the data obtained will not be displayed here. For constant PS–AP ratio, the V vs P curves in oxygen have the same shape as the PS bead curve

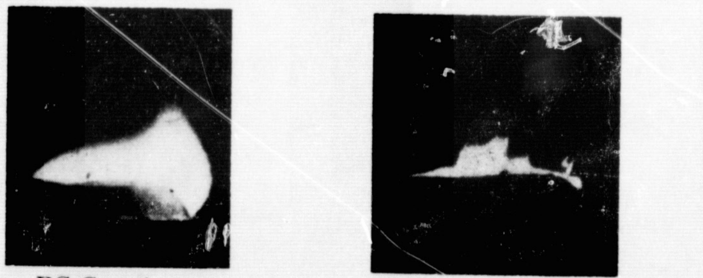

PS Specimen
PMM Specimen

Fig. 13 Flame spreading over igniting solid thermoplastic surfaces in 100% oxygen.

(Fig. 11), but the magnitude varies inversely with the weight fraction of AP. For example, at 10 in. of Hg, the wt AP/wt PS = 1 mixture produces a V of 0.13 in./sec., whereas the wt AP/wt PS = 3 mixture produces a V of 0.11 in./sec. As was anticipated, surface roughness effects resulted in a pressure exponent greater than unity.

Summary of Conclusions

An elementary flame-spreading experiment has been developed. The rate of flame spreading over the igniting surface of a variety of solid propellants and solid propellant ingredients has been measured as a function of specimen surface condition and conditions in the surrounding atmosphere. The flame-spreading velocity of all materials tested exhibited a power law dependence on both the pressure level and reactive species weight fraction of the surrounding atmosphere; both the power law exponent and coefficient increased with increasing surface roughness. Since the materials tested were so diverse in their nature, their exhibited common flame-spreading behavior is strongly suggestive of a common mechanism of flame spreading. The authors have concluded that the basic mechanism of flame spreading is essentially one of continuous gas-phase ignition.

By making a number of simplifying assumptions, an analytical prediction of flame-spreading velocity dependence on pressure level and reactive species weight fraction in the surrounding atmosphere was produced. The analytical solution is valid only when the surface is smooth—as predicted, the experimental power law exponents were less than unity for specimens with smooth surfaces. The analytically predicted dependence of flame-spreading velocity on gas-phase parameter variation was supported by the data obtained throughout the relatively limited range of testing. It is expected that the central feature of the flame-spreading phenomenon illuminated during the subject study—that is, its basic gas-phase nature—will be exploited in developing new approaches to: 1) the rational design of new motor ignition systems; 2) the selection of "fixes" to improve inadequate systems already under development; and 3) more realistic analyses of the performance of existing systems.

References

[1] Altman, D. and Grant, A. F., *Fourth Symposium on Combustion* (Williams and Wilkins Co., Baltimore, Md., 1950), p. 158.

[2] Cook, M. A. and Olson, F. A., "Chemical factors in propellant ignition'" Am. Inst. Chem. Engrs. J. **1**, 391 (1955).

[3] Ryan, N. W., Baer, A. D., and Salt, D. L., "Propellant ignition by high convective heating fluxes," *ARS Progress in Astronautics and Rocketry: Solid Propellant Rocket Research*, edited by M. Summerfield (Academic Press Inc., New York, 1960), Vol. 1, pp. 653–665.

[4] McAlevy, R. F., III, Cowan, P. L., and Summerfield, M., "The mechanism of ignition of composite solid propellants by hot gases," *ARS Progress in Astronautics and Rocketry: Solid Propellant Rocket Research*, edited by M. Summerfield (Academic Press Inc., New York, 1960), Vol. 1, pp. 623–652.

[5] Fishman, N. and Beyer, R. B., "Solid propellant ignition studies with high flux radiant energy as a thermal source," *ARS Progress in Astronautics and Rocketry: Solid Propellant Rocket Research*, edited by M. Summerfield (Academic Press Inc., New York, 1960), Vol. 1, pp. 673–692.

[6] Anderson, R., Brown, R. S., Thompson, G. T., and Ebeling, R. W., "Fundamental theory of hypergolic ignition for solid propellants," AIAA Preprint 63-514 (1963).

[7] Summerfield, M., Shinnar, R., Hermance, C. E., and Wenograd, J., "A critical review of recent research on the mechanism of ignition of solid rocket propellants," Princeton Univ., Aeronautical Engineering Lab. Rept. 661 (August 1963); also Astronaut. Acta (to be published).

[8] Price, E. W., Bradley, H. H., Jr., Dehority, G. L., and Ibiricu, M. M., "Theory of ignition of solid propellants," AIAA J. **4**, 1154–1181 (1966).

[9] McAlevy, R. F., III and Hansel, J. G., "Linear pyrolysis of thermoplastics in chemically reactive environments," AIAA J. **2**, 244–249 (1965).

[10] McAlevy, R. F., III, Lee, S. Y., and Magee, R. S., "The solid propellant ignition mechanism: A simple diagnostic experiment," Aeronaut. Acta **11**, 144–145 (1965).

[11] Parker, K. H., Wenograd, J., and Summerfield, M., "The ignition transient in solid propellant rocket motors," AIAA Preprint 64-126 (1964).

[12] deSoto, S. and Friedman, H. A., "Flame spreading and ignition transients in solid grain motors," AIAA Preprint 64-122 (1964); also AIAA J. **3**, 405–412 (1965).

[13] Paul, B. E., Lovine, R. L., and Fong, L. Y., "Propellant surface flame propagation in rocket motors," AIAA Preprint 64-125 (1964).

[14] Mitchell, R. C. and Ryan, N. W., "Flame spreading on solid propellant," AIAA Preprint 64-128 (1964); also J. Spacecraft Rockets **2**, 610–612 (1965).

[15] McAlevy, R. F., III, Magee, R. S., and Wrubel, J. A., "Flame spreading over the surface of double base propellants," AIAA Preprint 64-109 (1965).

[16] McAlevy, R. F., III and Lee, S. Y., "A porous plug burner technique for the study of composite solid propellant deflagration on a fundamental level and its application to hybrid rocket propulsion'" *AIAA Progress in Aeronautics and Astronautics: Heterogeneous Combustion*, edited by H. G. Wolfhard, I. Glassman, and L. Green Jr. (Academic Press Inc., New York, 1964), Vol. 15, pp. 583–608.

[17] Hermance, C. E., Shinnar, R., and Summerfield, M., "Ignition of an evaporating fuel in a hot oxidizing gas, including the effect of heat feedback," Astronaut. Acta **12**, 95–113 (1966).

[18] Summerfield, M., private communication, Princeton Univ. (November 1965).

[19] Crank, J., *The Mathematics of Diffusion* (Clarendon Press, Oxford, 1956).

[20] Spalding, D. B., "A theory of inflammability limits and flame-quenching," Proc. Roy. Soc. (London) **A240**, 283 (1957).

[21] McAlevy, R. F., III and Summerfield, M., "Ignition of double base solid rocket propellants," ARS J. **32**, 270 (1962).

[22] Pearson, G. S. and Sutton, D., "Ignition of composite propellant fuels by perchloric acid vapor," AIAA J. **4**, 954 (1966).

[23] Parker, K. H., Most, W. J., and Summerfield, M., "The ignition transient in solid propellant rocket motors," AIAA Preprint 66-666 (1966).

PART V

A CRITERION FOR SPACE CAPSULE FIRE HAZARD MINIMIZATION

A67-40110

A Criterion for Space Capsule Fire Hazard Minimization

ROBERT F. MCALEVY III*

AND

RICHARD S. MAGEE†
Stevens Institute of Technology, Hoboken, N.J.

THIS laboratory is engaged in a fundamental study of the mechanism of flame spreading over the surface of igniting solid materials.[1] Results have been produced that have implications concerning the fire hazard associated with oxygen-rich environments, as illustrated by the recent tragedies in the Apollo space capsule[2] and the Brooks Air Force Base School of Aerospace Medicine space capsule simulator.[2]

Two thermoplastics, polystyrene and polymethylmethacrylate, were tested in a chamber that was filled with O_2/N_2, O_2/He, and O_2/Ar mixtures having various oxygen mole fractions Y_{ox} at pressure levels P between 4 and 415 psia. Small specimens were ignited at one edge of the flat, top surface, and the velocity of flame spreading V over the surface was measured. Details of the experimental technique appear in Ref. 1.

A continuous, diffusive gas-phase ignition model of the flame spreading process has resulted in the prediction that the flame spreading velocity is "diffusion controlled" and thus would be affected by factors that influence molecular diffusion in the gas phase. A previous analysis of this model[1] has been improved recently by making more sophisticated assumptions. It results in an explicit dependence of V on P and Y_{ox} in the form

$$V \propto Y_{ox}{}^{m} P^{n} \tag{1}$$

All data obtained were precisely correlated on the basis of Eq. (1). It was determined that $m > 1$ and is a function of the diluent, and $n < 1$ and is relatively constant. Further, for the same environmental conditions, i.e., Y_{ox} and P, helium produced the fastest rate of flame spreading, nitrogen the slowest, while argon displayed an intermediate behavior.

Thus, as a consequence of the subject program, a rational basis for the selection of manned capsule environments has emerged for minimization of the rate of flame spreading following accidental ignition. For example, assuming that the combustible materials in the cabin exhibit flame spreading characteristics similar to the thermoplastics studied, Eq. (1) shows that an increase of oxygen partial pressure PY_{ox} is best achieved by increasing P rather than Y_{ox} (since $m > 1$ and $n < 1$) in order to minimize the associated increment in V. Further, if a two-gas system is employed, nitrogen is the best choice of inert diluent and helium the worst of the three tested. It is suggested that the announced decision[2] to employ a O_2/He environment for the U.S. Air Force Manned Orbital Laboratory be re-examined in light of these results.

References

[1] McAlevy, R. F., III, Magee, R. S., Wrubel, J. A., and Horowitz, F. A., "Flame spreading over the surface of igniting solid rocket propellants and propellant ingredients," AIAA J. 5, 265–271 (1967).

[2] Voss, K., David, H., and Taylor, H., "Special report: Apollo 204," Tech. Week 20, 12–17 (February 6, 1967).

Received June 19, 1967. This work was supported by NASA Grant NGR-31-003-014. [4.23, 12.01]

* Professor and Director of the Combustion Laboratory. Associate Member AIAA.

† Assistant Research Engineer, Combustion Laboratory.

4r 38 $46. N

Reprinted from JOURNAL OF SPACECRAFT AND ROCKETS

A Criterion for Space Capsule Fire Hazard Minimization

Robert F. McAlevy III*

and

Richard S. Magee†
Stevens Institute of Technology, Hoboken, N.J.

THIS laboratory is engaged in a fundamental study of the mechanism of flame spreading over the surface of igniting solid materials.[1] Results have been produced that have implications concerning the fire hazard associated with oxygen-rich environments, as illustrated by the recent tragedies in the Apollo space capsule[2] and the Brooks Air Force Base School of Aerospace Medicine space capsule simulator.[2]

Two thermoplastics, polystyrene and polymethylmethacrylate, were tested in a chamber that was filled with O_2/N_2, O_2/He, and O_2/Ar mixtures having various oxygen mole fractions Y_{ox} at pressure levels P between 4 and 415 psia. Small specimens were ignited at one edge of the flat, top surface, and the velocity of flame spreading V over the surface was measured. Details of the experimental technique appear in Ref. 1.

A continuous, diffusive gas-phase ignition model of the flame spreading process has resulted in the prediction that the flame spreading velocity is "diffusion controlled" and thus would be affected by factors that influence molecular diffusion in the gas phase. A previous analysis of this model[1] has been improved recently by making more sophisticated assumptions. It results in an explicit dependence of V on P and Y_{ox} in the form

$$V \propto Y_{ox}{}^{m} P^{n} \tag{1}$$

All data obtained were precisely correlated on the basis of Eq. (1). It was determined that $m > 1$ and is a function of the diluent, and $n < 1$ and is relatively constant. Further, for the same environmental conditions, i.e., Y_{ox} and P, helium produced the fastest rate of flame spreading, nitrogen the slowest, while argon displayed an intermediate behavior.

Thus, as a consequence of the subject program, a rational basis for the selection of manned capsule environments has emerged for minimization of the rate of flame spreading following accidental ignition. For example, assuming that the combustible materials in the cabin exhibit flame spreading characteristics similar to the thermoplastics studied, Eq. (1) shows that an increase of oxygen partial pressure PY_{ox} is best achieved by increasing P rather than Y_{ox} (since $m > 1$ and $n < 1$) in order to minimize the associated increment in V. Further, if a two-gas system is employed, nitrogen is the best choice of inert diluent and helium the worst of the three tested. It is suggested that the announced decision[2] to employ a O_2/He environment for the U.S. Air Force Manned Orbital Laboratory be re-examined in light of these results.

Received June 19, 1967. This work was supported by NASA Grant NGR-31-003-014. [4.23, 12.01]

* Professor and Director of the Combustion Laboratory. Associate Member AIAA.

† Assistant Research Engineer, Combustion Laboratory.

References

[1] McAlevy, R. F., III, Magee, R. S., Wrubel, J. A., and Horowitz, F. A., "Flame spreading over the surface of igniting solid rocket propellants and propellant ingredients," AIAA J. **5**, 265–271 (1967).

[2] Voss, K., David, H., and Taylor, H., "Special report: Apollo 204," Tech. Week **20**, 12–17 (February 6, 1967).

Reprinted from JOURNAL OF SPACECRAFT AND ROCKETS