N69-15387
NASA CR-99084

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

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Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
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GRANT NO. NGR-31-003-014
OCTOBER 1968
ANNUAL REPORT

STEVENS INSTITUTE
OF TECHNOLOGY

DEPARTMENT OF MECHANICAL ENGINEERING

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ANNUAL REPORT ME-RT 68008
OCTOBER 1968

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Washington 25, D. C.

Grant No. NGR-31-003-014

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PROLOGUE

The main body of this report is based on a paper by R. F. McAlevy, III and R. S. Magee, entitled "The Mechanism of Flame Spreading Over the Surface of Igniting, Condensed Phase Materials", that was presented at the Twelfth Symposium on Combustion (International) held at the University of Poitiers, France July 14-20, 1968. Appendecies A and B, not referred to in the main body, contain results obtained since then.

ABSTRACT

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 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

$$V \propto \left(P Y_{OX}^{m}\right)^{\Phi}$$

It is concluded that V is controlled by a gas-phase physical process--probably either heat or mass transfer.

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 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 can now be put on a rational basis.

TABLE OF CONTENTS

	Page
TITLE PAGE	
PROLOGUE	ii
ABSTRACT	iii
TABLE OF CONTENTS	v
LIST OF FIGURES	vi
LIST OF TABLES	vii
BACKGROUND AND INTRODUCTION	1
EXPERIMENTAL APPROACH	3
THEORY	5
RESULTS AND CONCLUSIONS	9
REFERENCES	16
APPENDICIES	
A. ICRPG REFERENCE PROPELLANT FLAME SPREADING CHARACTERISTICS	A-1
B. THE INFLUENCE OF FORCED CONVECTION ON FLAME SPREADING VELOCITY	B-1
TABLES	
FIGURES	

LIST OF FIGURES

Figure

1 Schematic of Apparatus for Flame Spreading Velocity Measurement

2 Processes Involved in Continuous Diffusive Gas-Phase Ignition Model of Flame Spreading

3 Log V vs Log P for Two Thermoplastics in O_2/N_2 Environments

4 Log V vs Log P for Two Thermoplastics in O_2/He Environments

5 Log V vs Log Y_{ox}^{3} P for Polymethylmethacrylate in O_2/N_2 Environments

6 Log V vs Log $Y_{ox}^{1.9}$ P for Polystyrene in O_2/He Environments

7 Typical Surface Temperature Profile

LIST OF TABLES

TABLE

I Experimental Values of Φ and m

II Experimental Values of q and r for Polymethylmethacrylate

III Calculated and Experimental Values of Φ and m for Polymethylmethacrylate

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. 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,[1,2,6,7,8]

, with the exception of the work produced in the authors' laboratory, there appears 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 inter-diffusion 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 on 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" x 3/8" x 1/8") were mounted, smooth 3" x 3/8" surface upwards, on backing plates (3-1/4" x 1/2") and burned in a relatively large test chamber (10" i.d. x 18") 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 check 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" x 3/8" surface upward, the chamber was sealed then evacuated and charged with the selected test gas to the pressure in the surge tank, thus opening the check valve. 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 3/8" 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" 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" edges and onto the top surface for a distance of about 1/32".

Flame spreading data were obtained for high spreading velocities from cinecamera records. Low spreading velocities (below about 0.1 in/sec.) were determined from stopwatch measurements of the time required for the flame to propagate a fixed distance (2"). 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 1/2" 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 diameter wire, 15 μ diameter bead, platinum, platinum-10%

rhodium). 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 2/3 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 produced. The recorder chart speeds employed were 2, 10 and 50 in/sec. depending on 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 Figure 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 describe completely flame spreading in a quiescent environment take the form of a set of four, unsteady very non-linear, 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:

$$V = \delta / t_{ig} \qquad (1)$$

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. 10,12 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 on 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 of the analyses have resulted in a predicted power-law dependence of t_{ig} on environmental pressure (P) and gas-phase reactive component mole fraction (Y_{ox}), that can be represented as

$$t_{ig} \propto (P\, Y_{ox}^{s})^{-\beta} \qquad (2)$$

where the values of s and β depend on the detailed nature of the subsidiary 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

$$V \propto \delta\, (P\, Y_{ox}^{s})^{\beta} \qquad (3)$$

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

$$\delta \propto (P\, Y_{ox}^{q})^{-r} \qquad (4)$$

then

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

$$V \propto (P\, Y_{ox}^{m})^{\Phi} \qquad (5)$$

where

$$\Phi = \beta - r \qquad (6)$$

and

$$m = \frac{s\,\beta - rq}{\beta - r} \qquad (7)$$

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 (0_2) and nitrogen (N_2), and the thermoplastics in mixtures of 0_2 and N_2, 0_2 and argon (Ar) and 0_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 0_2 and for PMM in mixtures of $0_2/N_2$, $0_2/Ar$ and $0_2/He$ 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.

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 which 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 on 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 of the data obtained to date in the authors' laboratory, which involves over 1,500 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 Figures 3 and 4 respectively. The measured flame 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

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

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. Despite 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 for 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. As 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 $\delta^{*} \propto (P\ Y_{ox}^{q})^{-r}$, 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 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 on 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, on 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 on 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 equations 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 $\beta < 1/3$. Since $r > 1/3$ 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 on P and Y_{ox} and allow 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 can not be made at this time. More information is required.

F. For the heuristic assumption of constant surface vaporization rate, a "zeroth-order" solution of the one dimensional, unsteady conservation equations for diffusive, gas-phase ignition results in the prediction $t_{ig} \propto P^{-1.44}$ according to Reference 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 that t_{ig} depends inversely on Lewis Number, as suggested by the analysis on pg. 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 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 the work of 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 result in successful prediction of flame spreading characteristics also. 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 on 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 in 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 Figure 7). It was found that within the limits of data scatter ($\pm$ 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"].
>
> During steady combustion of PMM with an impinging oxygen jet, the temperature at the vaporizing surface was found to be greater than 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 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]

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APPENDIX A

ICRPG REFERENCE COMPOSITE PROPELLANT FLAME SPREADING CHARACTERISTICS

Flame spreading velocity was measured for the ICRPG reference composite propellant. It is composed of 24% binder and 76% ammonium perchlorate. The binder formulation is a polyurethane using Estane 5720X5 (B.F. Goodrich) cured with a mixture of 10% 1,4 butanediol, 20% trimethylolpropane and 70% Polycin 51 (Baker castor oil). The propellant was tested in mixtures of oxygen (O_2) and nitrogen (N_2) of various levels of oxygen mole fraction (Y_{ox}) and total pressure (P). The experimental approach employed was basically that used in the previous flame spreading studies (as described in the body of the text).

The flame spreading velocity was measured at pressure levels between 4 and 415 psia in environments of Y_{ox} = .21, .65, 1.00 and in 100 percent nitrogen. Below 100 psia, all data exhibited the pressure dependence,

$$V \propto P^{1.15}$$

Above 100 psia the dependence on pressure was somewhat less. To date, insufficient data has been obtained in this region to permit extraction of a value for the pressure exponent.

Further, all of the data obtained in the O_2/N_2 mixtures below 100 psia could be correlated by an empirical power-law relationship between V and two gas-phase parameters P and Y_{ox}, in the form

$$V \propto (P \; Y_{ox}^{m})^{\Phi} \qquad \text{where} \qquad \begin{aligned} \Phi &= 1.15 \\ m &= 0.65 \end{aligned}$$

This functional relationship is identical to that obtained previously for double base propellants and thermoplastics typical of those used for ingredients in solid propellant fuels (pg.10). However in all other instances m > 1. This suggests that fuel vapors leaving the composite propellant surface react not only with oxygen initially present in the environment, but with pyrolyized oxidizer vapors as well. Thus while the continuous diffusive gas-phase ignition theory of flame spreading provides a basis for data correlation for composite propellants, the analysis must be modified to include the affect of pyrolyzed oxidant vapors. This is presently underway.

APPENDIX B

The Influence of Forced Convection on Flame Spreading Velocity

During ignition of most solid propellant rocket motors forced convective motion can exert a powerful influence on the flame spreading phase of the overall ignition transient. This factor is being studied experimentally.

Initially, the influence of forced convective motion on the flame spreading velocity was measured utilizing a low speed wind tunnel (0 - 20 fps). Test samples of a nitrate ester propellant were mounted a fixed distance behind the leading edge of a flat plate specimen holder. The forced convective motion of the air environment was, in one case, in the direction of flame propagation and, in another case, opposed to the direction of flame propagation. When the air velocity opposed the propagating flame two regimes of interest were apparent. For flow velocities greater than 10 ft/sec, the flame was blown off the surface and the sample underwent a steady deflagration. Below 10 ft/sec the flame spreading velocity increased with increasing flow velocity. For forced convection in the same direction as flame propagation there also exists two regimes. For low flow velocities, roughly 8 ft/sec or less, a distinguishable flame front spread across the sample surface; the flame spreading velocity increasing with increasing flow velocity. As the flow velocity was increased above 8 ft/sec., the flame plume was forced by the flow to lie on the surface of the specimen. And in this case it was impossible to discern the location of the propagating flame front. The limitation of the low speed wind tunnel to a small range of flow velocities (0 to 20 fps), the difficulties in accurately measuring the low flow velocities, and the inability to vary the gas composition (air) and temperature led the authors to design a new experimental apparatus.

The new test apparatus consists of an aluminum wind tunnel (1"x1" x 12") which is both driven and supplied by cylinders of the compressed test gas. For observation purposes, the walls of the test section were constructed of pyrex. The test sample is placed in the center of the floor of the test section (1" x 1" x 4") so that the exposed fuel surface (3/8" x 4") is flush with the floor of the tunnel. Ignition of the specimen was accomplished by means of an electrically heated wire positioned on the surface of an easily ignitable fuel charge (3/8" x 1/8") which then serves as the ignition source of the specimen. As in the case of a quiescent environment, it was found necessary to inhibit the edges of the fuel surface. The flame spreading rates were determined from timing clock measurements of the time required for the flame to propagate a fixed distance (2"). The flow velocity of the test gas was determined by utilizing a calibrated flowmeter.

Using this new apparatus, experimental tests were performed with forced convective motion opposed to the direction of the flame propagation over fuels of polymethylmethacrylate (PMM) and the ICRPG binder in 100% 0_2 environments. At present the flame has not been blown off the surface for flow velocities ranging from 0.6 fps to 7.4 fps for PMM, or for flow velocities ranging from 0.6 fps to 24.8 fps for the ICRPG binder. Both fuels exhibited increasing flame propagation rates with increasing flow velocities. And over the range tested, both sets of data could be correlated by an empirical power law relationship of the form $V_f \propto (V_a)^{0.36}$, where V_f is the flame velocity and V_a is the 0_2 flow velocity.

TABLE I

EXPERIMENTAL VALUES OF Φ and m

SPECIMEN	ENVIRONMENTAL COMPOSITION					
	O_2/N_2		O_2/He		O_2/Ar	
	Φ	m	Φ	m	Φ	m
PROPELLANT A	.62	2	–	–	–	–
PROPELLANT B	.65	2	–	–	–	–
POLYSTYRENE	.76	3	.80	1.9	.83	2.6
POLYMETHYL-METHACRYLATE	.82	3	.78	1.9	.78	2.6

TABLE II

EXPERIMENTAL VALUES OF q and r FOR POLYMETHYLMETHACRYLATE

ENVIRONMENTAL COMPOSITION	q	r
$0_2/N_2$	0	.50
0_2/He	1.0	.55
0_2/Ar	0.2	.60

TABLE III

CALCULATED AND EXPERIMENTAL VALUES OF Φ and m FOR POLYMETHYLMETHACRYLATE

		ENVIRONMENTAL COMPOSITION					
		$0_2/N_2$ (s=2.0)*		0_2/He (s=2.3)*		0_2/Ar (s=1.5)*	
	β	Φ	m	Φ	m	Φ	m
Calculated	1.44	.94	3.1	.89	3.1**	.84	2.4
Experimental		.82	3.0	.78	1.9	.78	2.6

* Calculated from Eq. 19, Ref. 13

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

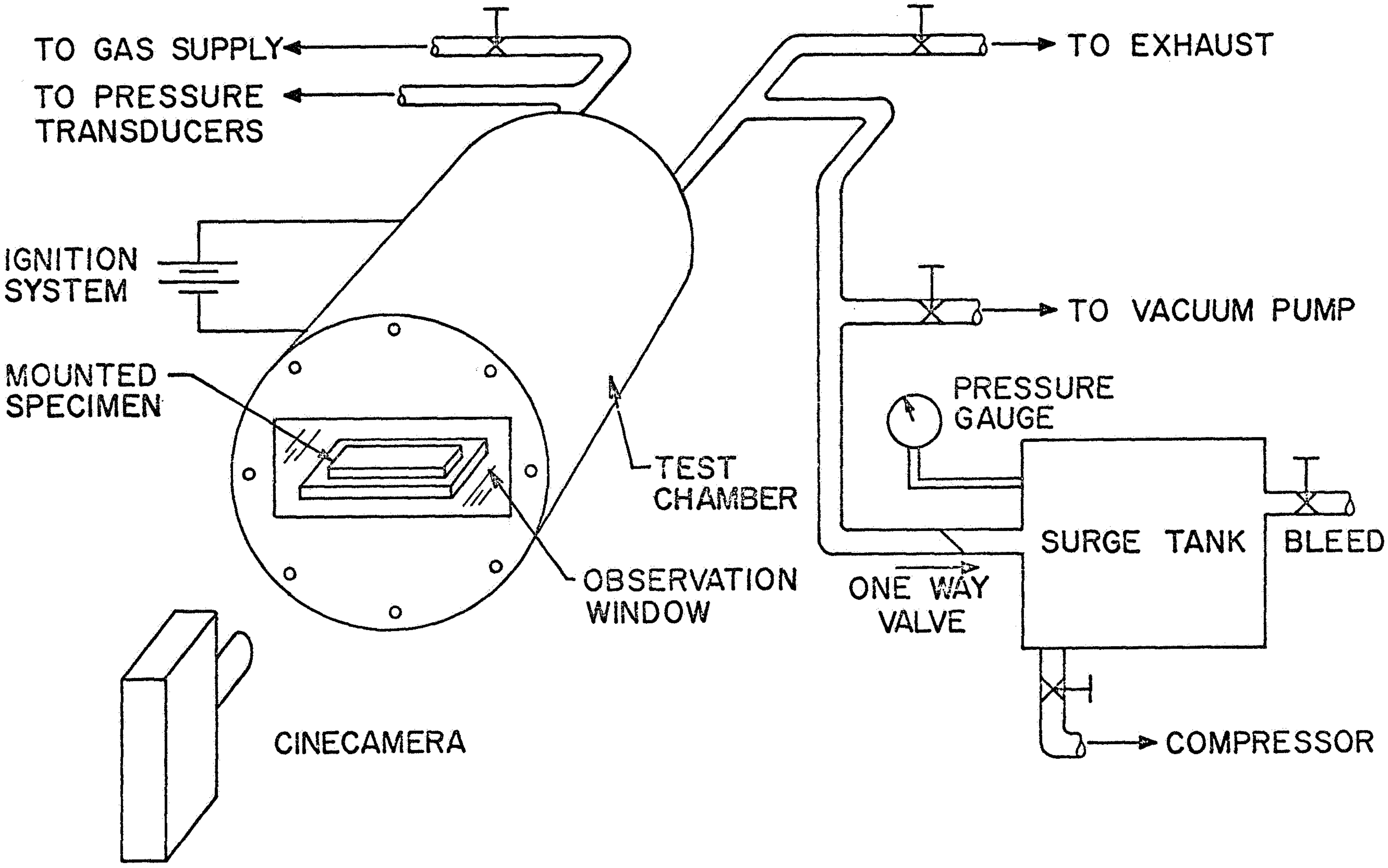

FIG. I SCHEMATIC OF APPARATUS FOR FLAME SPREADING VELOCITY MEASURMENT

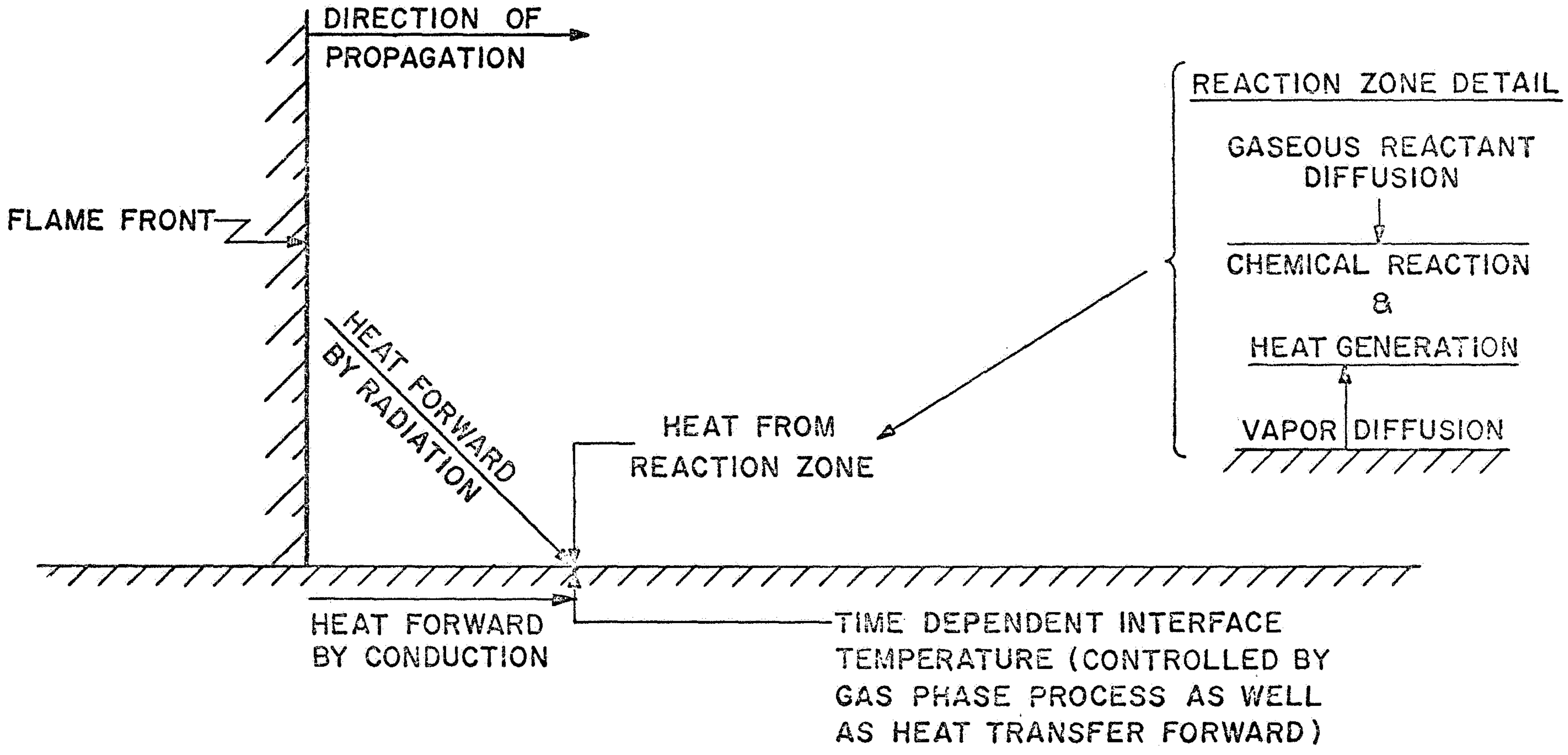

FIG. 2 PROCESSES INVOLVED IN CONTINUOUS DIFFUSIVE GAS-PHASE IGNITION MODEL OF FLAME SPREADING

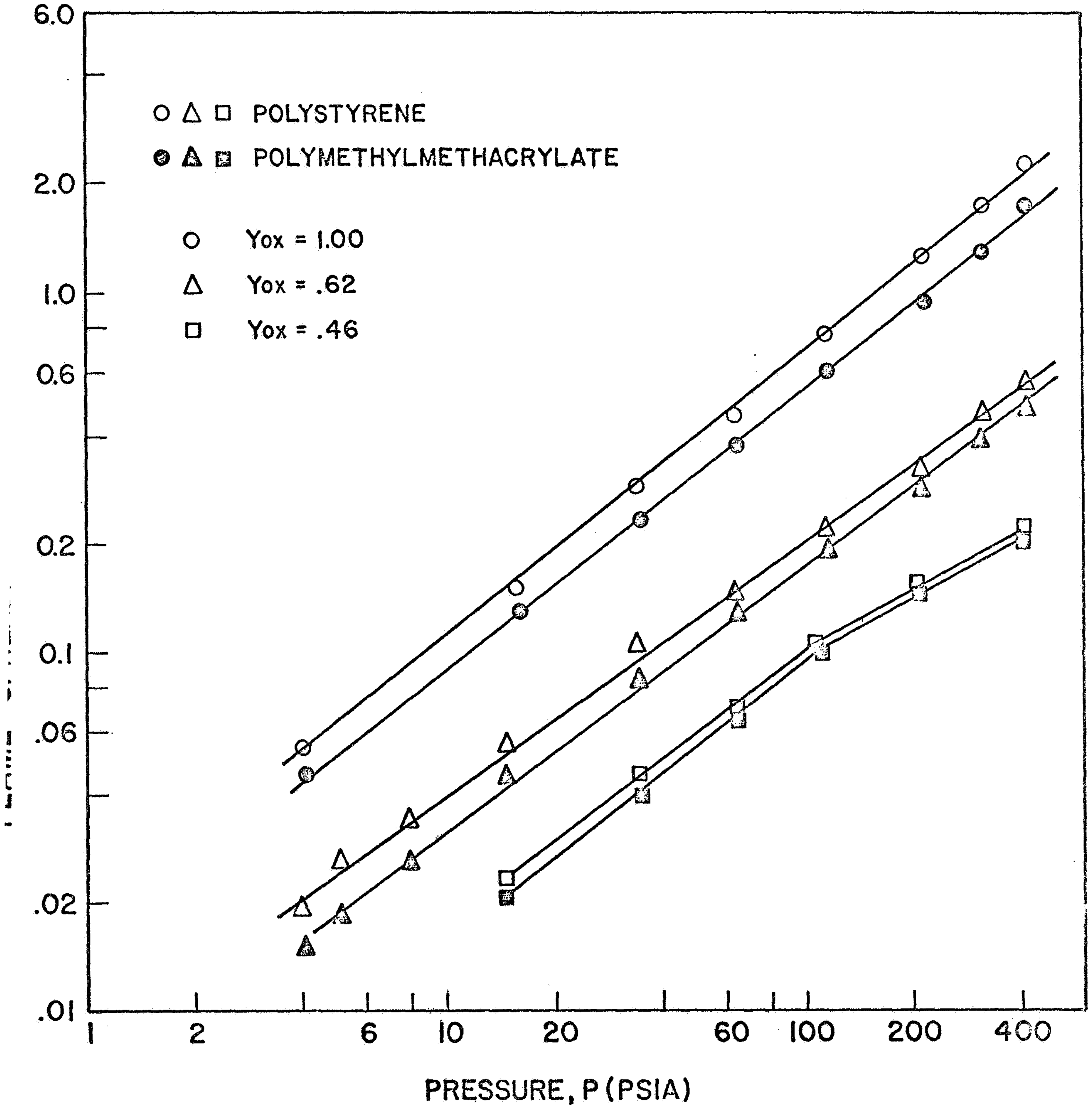

FIG. 3 LOG V VS LOG P FOR TWO THERMOPLASTICS IN O_2/N_2 ENVIRONMENTS

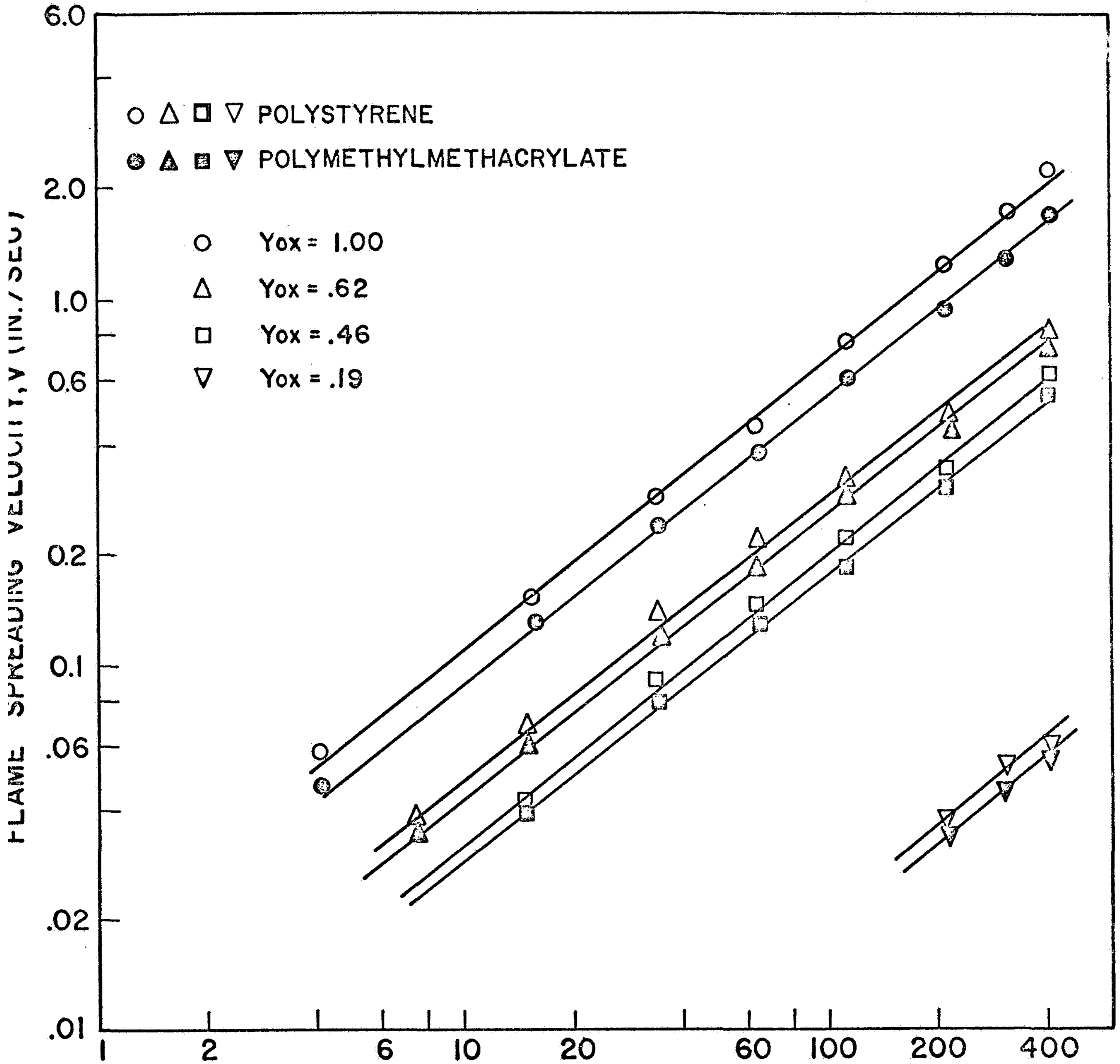

FIG. 4 LOG V VS LOG P FOR TWO THERMOPLASTICS IN O_2/He ENVIRONMENTS

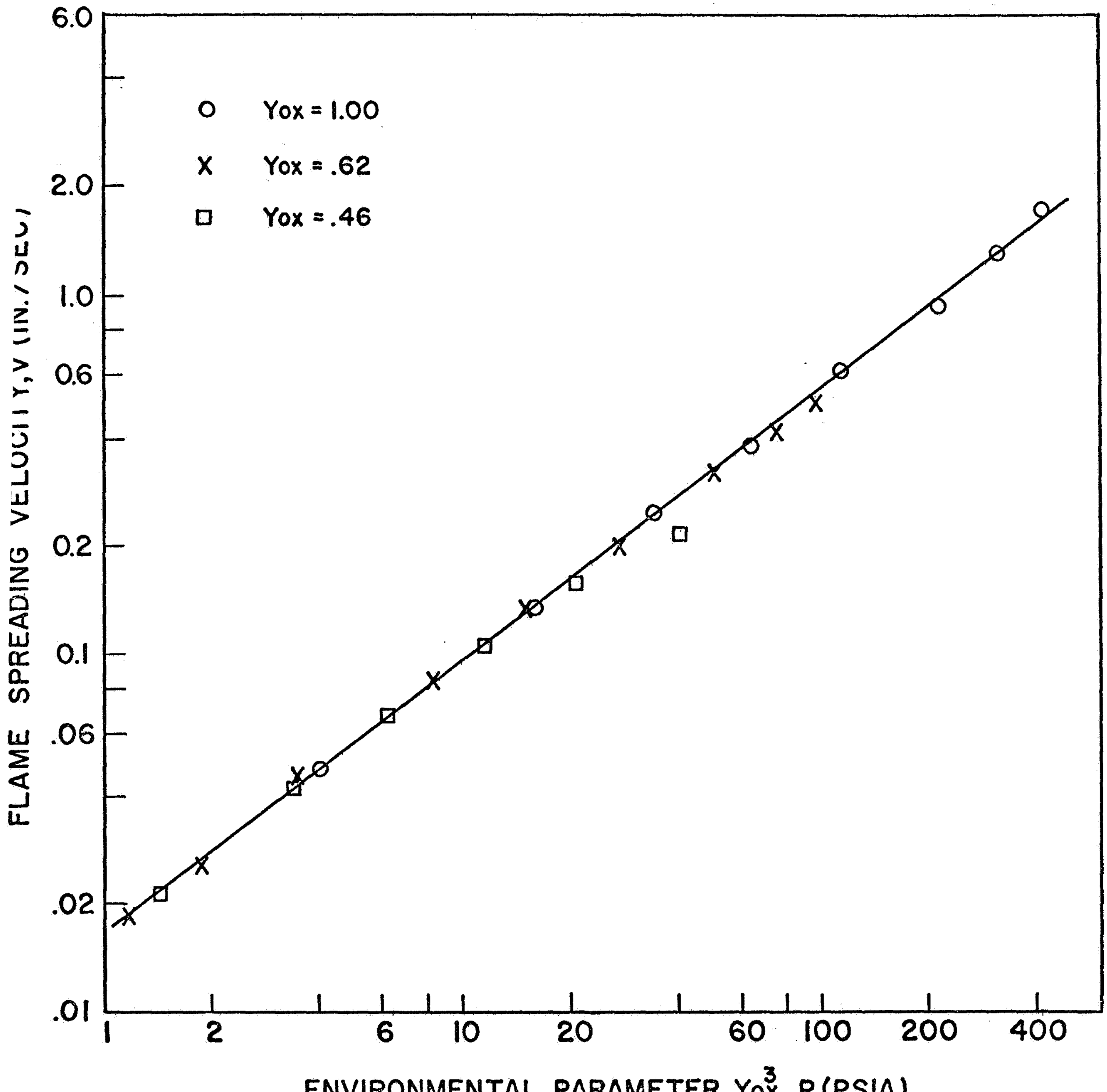

FIG. 5 LOG V VS LOG Y_{ox}^3 P FOR POLYMETHYLMETHACRYLATE IN O_2/N_2 ENVIRONMENTS

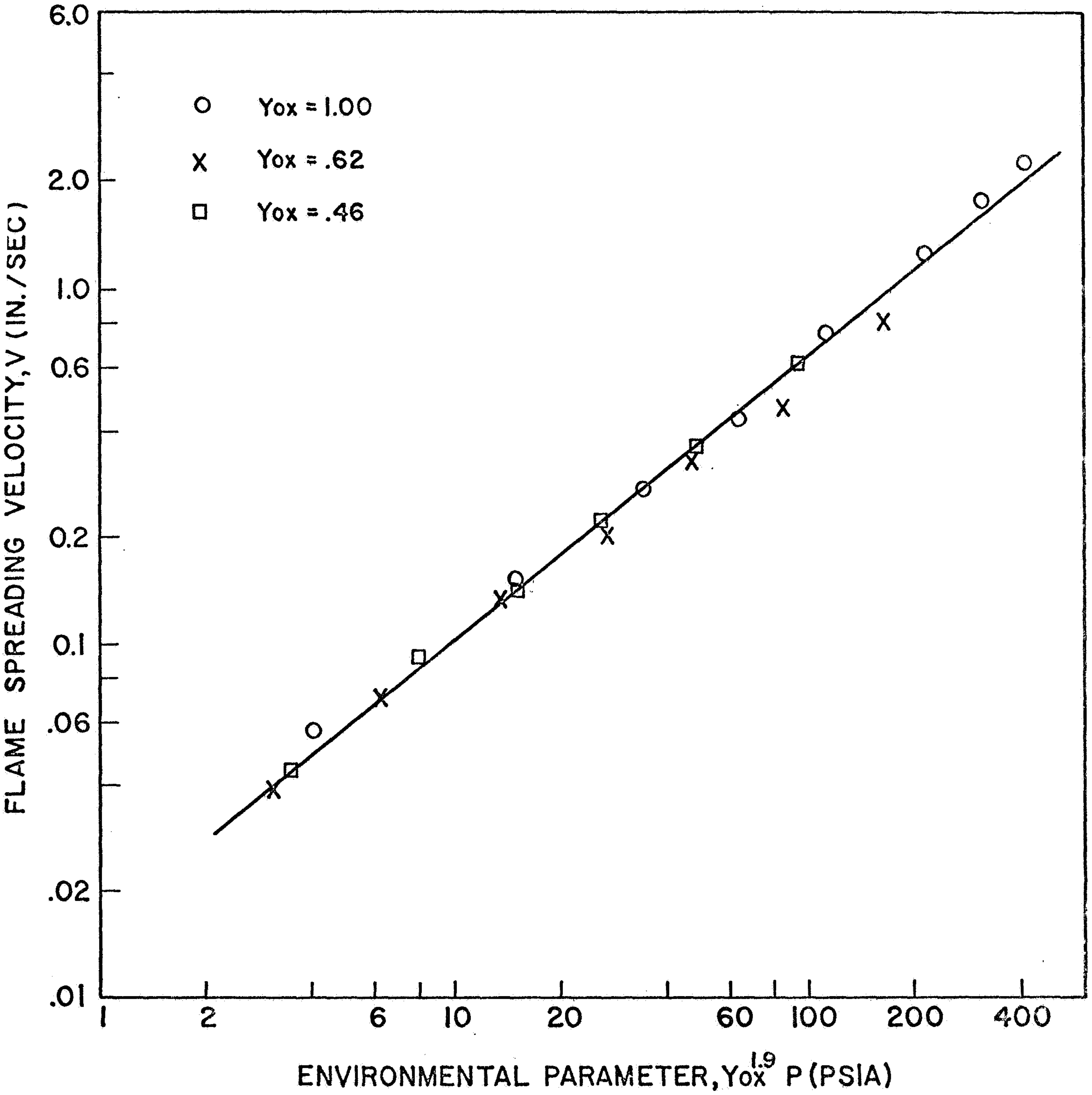

FIG. 6 LOG V VS LOG $Y_{ox}^{1.9}$ P FOR POLYSTYRENE IN O_2/He ENVIRONMENTS

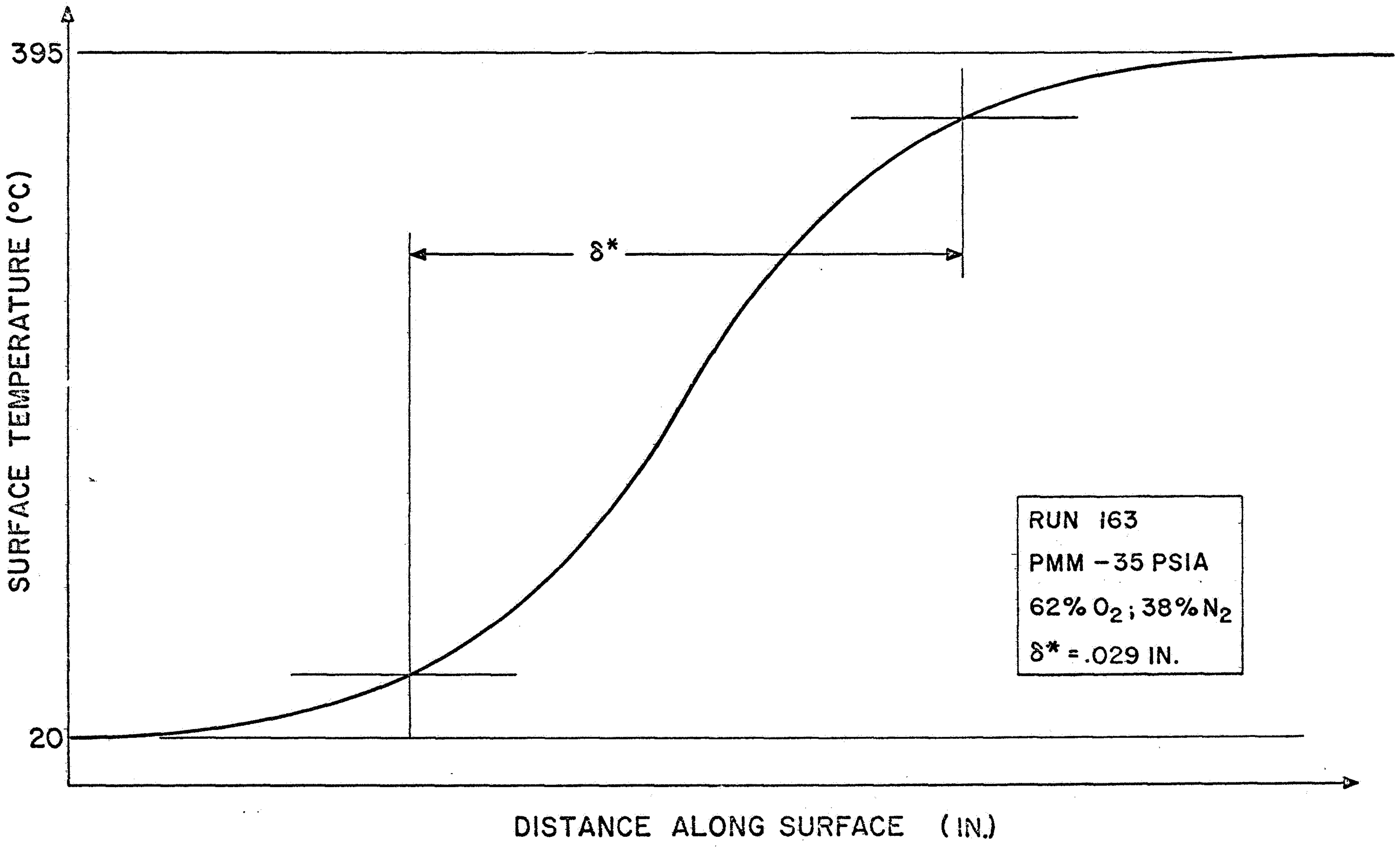

FIG. 7 TYPICAL SURFACE TEMPERATURE PROFILE