FLAME SPREADING OVER THE SURFACE OF DOUBLE BASE PROPELLANTS AT HIGH PRESSURE

by

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ABSTRACT

The velocity at which a flame spreads over the surface of igniting nitrate ester (double base) propellants of two different compositions has been measured Test parameters were pressure level and chemical nature of the surrounding quiescent atmosphere. Small test specimens, mounted horizontally, in a relatively large high-pressure test chamber were ignited and the flame spreading velocity was obtained cinematographically. Flame spreading velocity was found to vary: directly with pressure level (between 6 and 415 psia); and directly with the oxygen weight fraction in environments composed of oxygen-nitrogen mixtures. It was demonstrated that all data, except those taken in 100 percent nitrogen could be correlated by an equation of the form; $V \propto (Z^2P)^r$, where V is the flame spreading velocity, Z is the chemical reactivity of the surrounding environment, P is the pressure level, and r is a pure number approximately equal to 0.6. Flame spreading data taken in 100 percent nitrogen yielded velocities of the same order of magnitude as the linear burning rate; whereas in 100 percent oxygen at 415 psia the velocity was greater than the linear burning

rate by approximately a factor of 15! It is concluded that in reactive environments the mechanism of flame spreading is substantially different from that which controls surface linear regression during normal burning.

Although the results of the present experiments are generally consistent with the previously hypothesized gas phase model of flame spreading,[19] they are inconsistent with the results predicted by the previous theoretical analysis of the model. A discussion is presented of some of the assumptions underlying this analysis that might be unrealistic in so far as the present work is concerned.

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NOMENCLATURE

Symbol	
A	Arrhenius equation pre-exponential factor - - [(mass/unit volume)$^{-1}$/unit time]
C	Concentration - - mass/unit volume
C_p	Heat capacity/unit mass at constant pressure
E	Activation energy for the gas phase reaction
e	Exponential function
f	Function
m	Exponent, equal to $\frac{1}{n+1}$
n	Exponent, greater than one
P	Static pressure -- psia
$\dot{Q}_{chem}$	Chemical heat generation/unit mass
q	Chemical heat release/unit mass
R	Universal gas constant
r	Exponent
T	Temperature -- absolute
t	Time
V	Flame spreading velocity -- distance/unit time
X	Distance -- normal to surface
Z	Weight fraction, equals $\frac{wt\%O_2}{wt\%O_2 + wt\%N_2}$

Greek Symbols

$\propto$	Proportional to
ρ	Density -- mass/unit volume
τ	Ignition delay time

Subscripts

g	Gas
o	Initial
ig	Ignition

Superscripts

*	Ignition site

SECTION I

BACKGROUND

During the past decade the rapidly expanding utilization of solid propellant propulsion systems has given rise to a large number of solid propellant rocket motor ignition studies. Historically, motor ignition system design has been empirical; and despite this recent flourish of attention, it remains so even today. It is hoped, perhaps optimistically, that as a result of the flame spreading studies being conducted in this laboratory it will be possible to establish a basis for the rational design of ignition systems as far as flame spreading is concerned; or at least evolve a set of rules for the scaling of successful systems to meet the requirements of new applications. These rules, ideally, should make it possible to calculate the minimum weight of igniter charge that is perfectly matched to any motor while yielding an optimized ignition pressure transient, i.e. no excessive pressure rise or ignition delay. In addition, they should give ignition characteristics that are highly reliable over a wide range of operating conditions.

To facilitate analysis, the overall motor ignition process is described by three principal phases: (1) heating of the exposed grain surface to incipient

ignition conditions, with isolated flames developing at some locations; (2) spreading of the flames over the remaining surface; and (3) filling the chamber with propellant combustion products until the equilibrium chamber pressure level is reached. In many operational ignition systems the igniter continues to fire during the flame spreading and chamber filling phases. This necessitates that the igniter's influence be accounted for in any completely valid description of these phases.

Almost every type of operational solid rocket motor ignition system initiates combustion by heating the exposed surfaces of the propellant grain - the source of energy being the hot combustion products of the burning igniter material. A great variety of heating situations are possible depending upon the type of igniter employed. For example, the propellant surface might be exposed to a complex combination of conductive, convective, and radiative heating - with heat being generated by condensation of certain vapors, exothermic chemical reactions, etc.

In order to clarify the first phase, several elementary experiments have been designed to measure the response of the propellant to one or more of the many types of ignition stimuli. A number of ignition

techniques have been employed in this regard - hot wires,[1] shock tubes,[2,3] arc-imaging furnaces,[4] exposure to powerful oxidizing agents,[5,6] and many others.[7,8,9] These experiments have demonstrated that, in general, propellant ignition response is related to surface heating rate, pressure level, and chemical reactivity of the surrounding atmosphere.

Current interpretations of these results are divided into two schools: (1) that which considers the principal exothermic process leading to ignition to take place in the gas phase following some vaporization of propellant constituents; and (2) that which considers the principal process to take place at the solid (or liquid) - gas interface which then leads 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. Excellent review papers[10,11] have recently been published that discuss these interpretations in detail.

Recent experiments in this laboratory[12,13] lead to the following conclusion: 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;

but, it is highly unlikely that this mechanism is valid when less powerful oxidizing agents, such as O_2, are present.

The phase of motor ignition which has received the least attention is flame spreading from areas of first ignition to eventual coverage of the entire grain surface. During the ignition of small motors this phase is completed within a few milliseconds, but the enormous grain surface area of massive solid propellant space booster motors results in a protraction of this interval to about one second. It becomes, therefore, an item of considerable interest when precise firing schedules must be met, e.g. when these motors are "clustered". Also, it appears that the time for flame spreading might be the most difficult to reduce in the development of anti-missile missile boosters where promptness in achieving full motor ignition is at a premium. The flame spreading phase is the subject of this thesis and will be discussed in detail herein.

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 the igniter combustion and by the combustion of the propellant grain, and the rate at

which it is being expelled through the nozzle. This phase, coupled with a study of flame spreading in a convective environment, has been investigated by Summerfield,[14] et al.

SECTION II

INTRODUCTION

It has not been possible to establish a thorough-going fundamental understanding of the phenomenon of flame spreading over an igniting solid propellant surface. A number of studies have been reported.[14-19] However, the first four of these focused on the flame spreading phenomenon in situations that were sufficiently complex - principally due to the presence of strong forced convection - to preclude elucidation of the underlying mechanism. Only the last two,[18,19] which were studies conducted in this laboratory, attempted to solve the flame spreading problem without the initial added complexities introduced by motion of the environment. It is believed that this must be done first in order to gain a fundamental understanding of the detailed mechanism of the process before a rational attempt can be made to solve the complex problem, i.e. flame spreading in a dynamic environment.

These studies utilized an elementary laboratory experimental technique designed to measure, in a quiescent atmosphere, the response of flame spreading velocity to various environmental conditions. They bore the same relationship to the second phase of motor ignition as the elementary ignition experiments.[1-9]

bore to the first phase. The results were strikingly similar to results obtained in ignition experiments[20] made with the same propellants. That is, it was demonstrated that flame spreading velocity depends strongly on pressure level, chemical nature of the surrounding quiescent atmosphere, and specimen surface condition. These findings were consistent with a postulated gas phase mechanism for the flame spreading process.

Recently, a study of flame spreading on space cabin materials has been reported;[21] the experimental approach is almost identical to that employed in this laboratory.[18,19] Unfortunately, the only published data contain a large degree of scatter. This precludes meaningful comparison with the work of this laboratory.

All previous experiments in this laboratory were conducted at atmospheric pressure and below. These provided a foundation for the design of the subject experiments, during the execution of which it was possible to gather flame spreading data at pressures up to 415 psia in environments composed of mixtures of oxygen and nitrogen. In order to allow open publication of the composition of the propellants tested, two were selected that were about to be declassified. These propellants were of the nitrate ester (double base, or homogeneous) type as were the three classified propel-

lants employed previously. Unfortunately, these two new propellants have not been declassified so their compositions can not be revealed herein.

Results of the previous studies of this laboratory were consistent with the proposed gas phase mechanism of flame spreading. The present work was designed to yield experimentally the dependence of flame spreading velocity on pressure level, for a pressure range approaching two orders of magnitude. The correlation of these data by means of the result of an analytical prediction based on the gas phase mechanism of flame spreading will be indeed a severe test of the mechanisms validity. In addition, these data should be of practical importance as they will be obtained near the operating range of a large variety of currently utilized solid propellant rocket motors.

SECTION III

DESCRIPTION OF APPARATUS AND TEST PROCEDURES

Each small test specimen (3" x 3/8" x 1/16") was mounted on (3 1/4" x 1/2") aluminum plates and was placed in a relatively large test chamber (10"i.d. x 18"). The sample was oriented with the surface to be burned parallel to the floor. After the chamber was sealed and charged with test gas, the specimen was ignited by an electrically heated wire placed along the top edge. The flame spreading was recorded by means of a motion picture camera. This experiment completely eliminated the complication of forced convective effects on the flame spreading process. Also, due to the size of the chamber and lack of nearby objects, convective currents produced by the flame had a negligible effect on the flame spreading process. Pressure increase of the surrounding atmosphere during flame spreading was reduced to a negligible level by having a large surge tank (10 cu. ft.) connected to the test chamber by a one-way valve. An unobstructed view of the phenomenon within the chamber was provided by an observation window, through which the event was filmed (Figure 1).

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 to the surface with plastic cement. To prevent the flame from spreading too rapidly 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 of the latter process - it was necessary to inhibit the edges of the specimen. An inorganic cement, consisting of asbestos and water glass in a weight ratio of 1:5 was applied to the sides of these specimens. This produced, when dried, a firmly bonded protective coating. Further development demonstrated that the effectiveness of the inhibition could be improved by extending the side coating over the edge and onto the top for a distance of about 1/32". All of the data reported herein were obtained with specimens inhibited in this manner.

Early experiments performed with 100 percent oxygen at 415 psia produced combustion of the ignition circuit copper lead wire. Analysis of the film of the event indicated that the glowing hot nichrome ignition wire would burn after it had ignited the propellant. The sparks emitted by the burning nichrome wire ignited the copper lead wires, which burned vigorously. This problem was resolved by encasing the copper lead wire in ceramic

sleeves and using nichrome wire of fine (.010 in.) diameter. Immediately following propellant ignition the fine nichrome wire fissured, and with the circuit broken the spark emission was almost completely eliminated.

In order to run at a selected test pressure, the surge tank was pressurized to the desired level with compressed air. After mounting a specimen in the chamber, the chamber was bolted tight then evacuated and charged with the selected test gas. At low pressures (below 65 psia) evacuation and charging were repeated 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 level of that in the surge tank, thus opening the one-way valve. Following this, the chamber pressure rose at an imperceptible rate while the test gas charging was continued. After allowing the chamber gas to become quiescent, the camera was started and the ignition circuit was closed.

The event was recorded on Kodak Tri-X 16 mm motion picture film (Figure 2). Either a low speed or a high speed cinecamera was used depending on the testing condition. The low speed camera (Bell and Howell, 16mm Model 70-DL) exposed at a calibrated rate of 71.6 frames/second, recorded the event for pressures below 215 psia for all

test gases but for all pressures for test gases with equal to 0.23 and zero. The high speed camera (Kodak High Speed Camera, 16 mm Serial No. 1812) exposed at approximately 300 frames/second, was used for pressures of 215 psia and above for test gases having a value of Z greater than 0.23. Following film development a motion analyzer (Vanguard, Model M-16) was employed to obtain the flame spreading velocity, i.e., the measured propagation distance per selected frame interval for the low speed camera, or per a selected number of 120 cycle/second timing marks for the high speed camera.

SECTION IV

EXPERIMENTAL RESULTS AND DISCUSSION

The two types of nitrate ester (double base) propellants tested were obtained through the kindness of J. P. Picard, R. G. Wetton, and R. F. Jasinski of the Propellant Laboratory, FREL Division, Picatinny Arsenal, Dover, New Jersey. They are designated here as Propellants A and B, in order of descending nitroglycerine-to-nitrocellulose ratio contained by each. (The exact compositions cannot be revealed here.)

Previously, experiments[18,19] were performed with propellant specimens that were received in the form of 3/8" diameter strands (rods) which required cutting along the axis to generate a flat surface and polishing of this surface to insure reproducibility of results. The present samples were received in the form of rolled flat sheets.

An experiment was conducted to compare the flame spreading velocity over a rolled surface to that of a polished surface. The results were: (1) no detectable difference in flame spreading velocity was obtained; but (2) the data scatter was slightly lower with the rolled surface. Therefore, no surface treatment was performed on the propellant samples used in this experiment.

The flame spreading velocity in the longitudinal direction was measured at pressure levels of 6, 15, 65, 115, 165, 215, 315, and 415 psia; and in chemical environments of 0.23, 0.57, 0.86, 1.00 weight percent oxygen in nitrogen, and in 100 percent nitrogen. These conditions were selected so that results could be readily compared with predictions of a previous analysis of the gas phase mechanism of flame spreading: the spreading velocity was predicted to be a function of both pressure level and chemical reactivity of the surrounding atmosphere (see Appendix I).

In general, it was observed that as the flame spreads across the igniting propellant surface three distinct regimes could be identified: (1) an initial period of unsteady spreading of very short duration; (2) a pseudo steady-state condition in which the flame front propagated uniformly to approximately 1/3 to 1/2 of the length of the specimen; and (3) a true steady-state condition as the flame propagated uniformly, but at a somewhat higher velocity, to the end of the specimen.

Figures 3 and 4 are "wave diagrams" (distance spread vs time plots) typical of the data in general. The transition between the pseudo steady-state and true steady-

state regimes usually, but not always, occurred at a well-defined "breakpoint" (Table 1). The breakpoint was always encountered in the first half of the specimen length. Therefore, to insure that the true steady-state information was obtained, data were recorded only for flame spreading over the second half of the specimens. Here the uniformly propagating flame front was always perpendicular to the long edge of the specimen. All data obtained in this manner were within $\pm$ 5 percent of the best fit curve drawn through the arithmetic mean points.

The previously developed analysis, from (Equation 9) Appendix I, predicts:

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

where m is a constant having a value less than 1. When the data for both propellants are plotted as log V vs log P (Figure 5), general agreement with this prediction is evident for the slopes are less than 1. The flame spreading velocity is not a smooth function of pressure. At values of $Z > 0.57$ the slope increases, while for $Z < 0.57$ the slope decreases. In order to clarify the nature of this behavior it would be necessary to take data at much higher pressures. Unfortunately, the present apparatus is limited to pressures of 415 psia, thus it

was impossible to do so during the present program.

When the data were plotted as log V vs log Z (Figure 6) the results were inconsistent with the prediction of $m < 1$. These data, in general, are well represented by straight lines, except for those obtained at 15 psia (for all Z) and above Z = 0.86 (for all pressures). The behavior of both propellants at 15 psia is similar to that obtained earlier in this laboratory[19] with three other nitrate ester propellants.

The present data yielded results that deviated in certain respects from those of the previously generated, and admittedly very crude,[19] analysis of the gas phase mechanism of flame spreading. However, insufficient time was available to produce an improved analysis. Instead, empirical correlations of the data were sought that might guide further analysis. Figures 7 and 8 display the excellent correlation of almost all of the data with Z^2P, with the exception of those obtained with propellant A which deviated from a straight line at the highest values of Z^2P tested. The only data that could not be correlated in this manner were obtained in nitrogen (Z = 0).

The burning rate (linear surface regression rate) produced by normal full-scale combustion of propellant B

was measured in a nitrogen environment by means of a Crawford Strand Burner Bomb. These data[22] were obtained through the kindness of Mr. O. A. Colitti of the Picatinny Arsenal. The burning rates were approximately 15 percent below the flame spreading rates obtained in nitrogen (displayed in Figure 5). Further, observation of the nature of the propellant surface character during flame spreading in nitrogen indicated that the process involved is merely normal burning of a planar surface oriented at an angle slightly greater than 90° with the top surface. Thus it appears that in nitrogen atmospheres the flame spreading velocity is equal to the normal burning velocity divided by the sine of the angle between the top surface and the plane of burning.

Flame spreading in chemically reactive environments, on the other hand, appears to differ in its essential nature from flame spreading in nitrogen. Figure 9 displays the different character of the spreading flame structure in chemically reactive vis-a-vis inert environments.

The nature of the mechanism by which a flame spreads over an igniting propellant surface appears to be essentially gas phase. That is, the important exothermic chemical reactions that drive the flame across the surface

take place in the gas phase following vaporization of some propellant surface material. The importance of the gas phase aspect of the phenomenon is illustrated by the data plotted in Figures 7 and 8 for both propellants. The flame spreading velocity is proportional to the environmental parameter, Z^2P, raised to the 0.6 power, even though their chemical compositions are quite different.

SECTION V

DISCUSSION OF THEORY

The phenomenon of flame spreading over an igniting propellant surface in a chemically reactive environment is viewed herein as one of continuous ignition; thus, the flame spreading and ignition processes are inextricably linked. 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 front. The elements immediately ahead of the front are at a condition of incipient ignition with ignition delay increasing monotonically with increasing distance from the flame.

Surveys[11] of current opinions on the solid propellant ignition phenomenon, as well as certain results recently obtained in this laboratory,[12,13] indicate 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 heat 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 research program and is not included in the model presented in Appendix I.

The elucidation of the gas phase mechanism of solid propellant ignition was evolved from conductive heating experiments.[3] 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.[3]

Utilization of computer techniques was required to obtain solutions that were better approximations.[23] At present, and for the first time, the gas phase mechanism of solid propellant ignition is being investigated analytically for convective heating.[24] However, theoretical analysis of the flame spreading phenomenon is materially more difficult. The analysis involves the interaction between the mutually perpendicular forward heat flux from the moving flame and the stream of propellant vapors which rise up from the surface. Whereas, in the analogous ignition situation[3] the heat flux from a still gas environment and the propellant vapor flux are parallel. Therefore, it should be expected that the first analysis of the gas phase flame spreading mechanism will be on an even more primitive level (see

Appendix I) than that of the gas phase ignition mechanism.

The experimental results presented herein, which cover an extremely wide range of experimental variables, lend support to the gas phase model of flame spreading. However, the primitive analysis of the model that has been produced appears to be based on assumptions that misrepresent somewhat the detailed processes within the general gas phase framework.

In light of the present work it seems necessary to make a reappraisal of the assumptions underlying the analysis. The most suspect of these appear to be:

(1) the distance ahead of the approaching flame which is affected by the presence of the front (thermal layer thickness) is constant,

(2) the distance above the surface, X*, at which temperature runaway occurs is constant, and

(3) the chemical reaction between propellant vapors and test gas -- the only reaction considered in this analysis -- is second order.

Flame temperature shows a minor dependence upon pressure but can have a major dependence on the chemical reactivity of the surrounding atmosphere for underoxidized propellants; hence, as the value of Z increases

the heat transfer forward can increase due to the elevated flame temperature. It appears that the thermal layer thickness is not constant but can be a function of Z. This is possibly the root of the multiplicative Z term missing from the analysis. No fundamental understanding of the above is possible until heat flux and temperature distributions in front of the flame are established so that the mode or modes of heat transfer forward can be rationalized.

Assumption (2) appears to be cogent based on earlier developments in this laboratory that demonstrated analytically that X* is not sensitive to variations of P; but, X* as a function of Z has never been checked and could be the source of the missing multiplicative Z term. The experimental determination of the dependence of X* on P and Z would require unavailable pyrolysis data for double base propellants. For the present this assumption has to be taken as heuristic, recognizing that it could possibly be the cause of the discrepancy between the previously developed analysis and this experiment.

In utilizing assumption (3) the possibility that the rate controlling step in the propellant combustion kinetics might be dependent on P and/or Z cannot be

ignored. However, the investigation of this possibility is outside the scope of the present work.

Experimental evidence demonstrating a dependence of the flame character on P and Z is shown in Figure 9. Within the framework of the underlying assumptions, the flame shape should not change; this clearly is not the case.

The elucidation of the aforementioned phenomena is beyond the scope of this research. The purpose in presenting this discussion is to report the observed effects and attempt to point out necessary areas of future research concentration.

SECTION VI

SUMMARY AND CONCLUSIONS

An elementary flame spreading experiment in a quiescent environment at high pressure has been performed. The rate of flame spreading over the igniting surface of two solid rocket propellants has been measured under various conditions of pressure and chemical reactivity of the surrounding atmosphere. The flame spreading velocity exhibited a power law dependence on the environmental parameter, Z^2P. It was demonstrated that all data, except those taken in 100 percent nitrogen, could be correlated by an equation of the form $V \propto (Z^2P)^r$, where $r \approx 0.6$. Flame spreading data taken in nitrogen yielded velocities approaching those of the linear burning rate. It is concluded that in inert environments what appears to be flame spreading is merely normal deflagration of a plane oriented at an angle slightly greater than 90° with the surface of interest.

Analysis of the experimental results confirms the basic hypothesis developed in this laboratory: flame spreading in a chemically reactive environment is a continuous gas phase ignition process. However, some of the results deviated from the predicted behavior

which was based on a crude analysis of the gas phase flame spreading mechanism. This suggests that some of the simplifying assumptions underlying the analysis might somewhat misrepresent certain details of the actual process,

With the fundamental knowledge gleaned from this and previous flame spreading experiments, it becomes possible, for the first time, to develop a rational analysis of the flame spreading phase of the solid propellant rocket motor ignition process. It is to be noted, however, that motor flame spreading takes place much more rapidly than those reported herein; but this is mainly due to the violent convective effects that are present during motor ignition. These effects were deliberately excluded from the present work. Now that some understanding of the fundamental mechanism of flame spreading has been attained, it should be possible to design a research program to elucidate the detailed nature of propellant flame spreading in a convective environment.

SECTION VII

RECOMMENDATIONS FOR FUTURE RESEARCH

As reported herein, an experimental investigation of the validity of the gas phase theory of flame spreading at high pressure on a fundamental level was conducted. An empirical equation is presented that correlates all data quite well except those obtained in nitrogen. However, flame spreading in the normal sense can not occur in an inert atmosphere. The empirical equation can not be derived from the previously developed analysis.[19] No consistent *a priori* reason could be formulated to account for this behavior. Future theoretical advance in this area must produce results that explain the present data, and it is recommended that this commence with an extensive review and experimental verification of the assumptions underlying the analysis; in addition, this review should consider the all important boundary condition of propellant phase change produced by surface heating.

An obvious extension of the present program would be to study flame spreading at high pressure with a wider variety of test specimens. These should include additional types of nitrate ester propellants, composite propellants, and metallized propellants of both types.

Also, the flame spreading characteristics of composite propellant ingredients (fuels in oxidizer environments and oxidizers in fuel environments) at elevated pressures should be studied. These data would provide a wealth of information on the characteristics of flame spreading for an extremely large number of practical propellants and would provide a means for checking the validity of theories as they are developed; however, these data probably will not be useful as a means of elucidating the basic mechanism. The author recommends that diagnostic experiments and detailed study of some of the underlying assumptions be undertaken for this purpose.

In order to rationalize the inherent transient before establishment of the "steady state" flame spreading velocity, information about the heat flux and temperature distributions ahead of the spreading flame front is required. Rapid response thin film heat flux gauges and fine thermocouples placed on the propellant surface will enable calculation of these distributions. By judicious choice of the type and placement of the heat flux gauges integrated with a systematic testing program, it should be possible to determine the magnitude and modes of heat transfer as well as its dependence

on pressure and chemical reactivity of the environment. For example, these data would be useful in determining if the thermal layer thickness is indeed constant, as was assumed during previous analytical treatment of the gas phase mechanism of flame spreading.

To make some realistic evaluation of how the distance above the surface where temperature runaway occurs, X*, varies with pressure and chemical reactivity, information on the concentration profiles and surface pyrolysis rate must be gathered. Surface pyrolysis data for double base propellants are non-existent, as far as the author knows. Recently in this laboratory a technique has been developed for obtaining pyrolysis data for thermoplastics.[12] Utilizing these together with concentration profile data[25] for the thermoplastic material as a function of pressure and chemical reactivity of the surrounding atmosphere, X* for these conditions might possibly be evaluated. Then, it may be possible to make some estimate of the variation of X* for double base propellants by extrapolating these data.

This program indicated a possible change in the order of the chemical reaction near 415 psia. To rationalize this change, data at higher pressure are required. This would necessitate a modification of the

existing high pressure flame spreading apparatus by the installation of a surge tank capable of withstanding higher pressure. Data can be taken as described in the text.

Finally, the forced convection of hot combustion gases past the propellant surface occuring in actual rocket motors significantly affects flame propagation. Any study of flame spreading must ultimately include these effects and future investigators should conduct dynamic flow experiments where the flame spreading velocity may be measured as a function of gas velocity, gas temperature, chamber pressure, etc.

SECTION VIII

THE AUTHOR'S ORIGINAL CONTRIBUTIONS

The original contributions of the author to this continuing flame spreading research program are:

(1) The construction of an apparatus to obtain data for flame spreading at high pressure.

(2) The gathering, for the first time, of flame spreading data in a quiescent atmosphere near the practical operating range of solid propellant rocket motors.

(3) The development of a correlation of flame spreading velocity with a parameter composed of a grouping of environmental test gas characteristics (pressure level and oxygen concentration).

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APPENDIX I

ONE-DIMENSIONAL MODEL OF FLAME SPREADING

Presented herein is the simplified gas phase theory of flame spreading developed in this laboratory[19] to describe this phenomenon on a fundamental level.

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

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

(2) The distance above the surface, X*, at which temperature runaway occurs -- the principal exothermic process leading to ignition takes place in the gas phase -- is 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 from when the flame presence is felt, and n is a positive constant. (See Reference 26 for exact solutions to the controlling 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 the site.

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

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

$$\rho C_p \frac{\partial T}{\partial t} = \dot{Q}_{chem} \quad . \qquad (1)$$

Within the framework of the assumptions the chemical heat generation rate per unit mass, $\dot{Q}_{chem}$, may be represented as:

$$\dot{Q}_{chem} = q(C)_{X*} C_g A e^{-E/RT} \quad . \qquad (2)$$

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

$$\dot{Q}_{chem} \propto q(\rho t^n) C_g A e^{-E/RT} \qquad (3)$$

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

$$\rho C_p \frac{\partial T}{\partial t} \propto q\rho^2 Z t^n A e^{-E/RT} \quad . \tag{4}$$

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

$$\left[\frac{RC_p T}{qAe^{-E/RT}} \right] \frac{\partial T}{\partial t} \propto ZPt^n \quad . \tag{5}$$

All terms within the brackets are physical constants, except T; therefore, we can represent the bracket as a function of T only, say f(T). Thus, (5) takes the form:

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

The limits of integration are:

$$t = 0 \text{ for } T = T_o$$

$$t = \tau \text{ for } T = T_{ig} \quad .$$

Then, (6) becomes

$$\int_{T = T_o}^{T = T_{ig}} f(T)dT \propto ZP\tau^{n+1} \quad . \tag{7}$$

Assuming both T_o and T_{ig} to be constant, (7) becomes:

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

Now, remembering that: (a) τ is the interval from the instant at which the advancing flame first produces

a significant effect at a certain location to the instant at which ignition of the propellant vapors occurs at that location; and (b) the distance ahead of the flame that is affected by the presence of the front is assumed to be constant ; then the flame spreading velocity, V, must vary inversely with τ. That is:

$$V \propto \frac{1}{\tau} \propto (ZP)^{\frac{1}{n+1}} \quad . \qquad (9)$$

Thus, this simplified analysis predicts a power law dependence of V on Z and P with an exponent, $m \equiv \frac{1}{n+1}$, where n is always positive, having a value less than unity.

TABLE 1

TYPICAL BREAKPOINT DATA FROM DISTANCE SPREAD VS TIME PLOTS

Propellant	Z	P (psia)	Slope Change Rel. Mag.	Time (sec.)	Distance (in.)
A	1.00	415	medium	0.25	1.2
A	1.00	315	medium	0.30	1.0
A	1.00	215	medium	0.60	1.6
A	1.00	115	large	0.90	1.7
A	1.00	15	small	0.72	1.5
A	0.57	415	large	0.55	1.0
A	0.57	215	medium	1.30	1.7
B	1.00	315	small	0.35	1.3
B	0.57	215	none	----	---

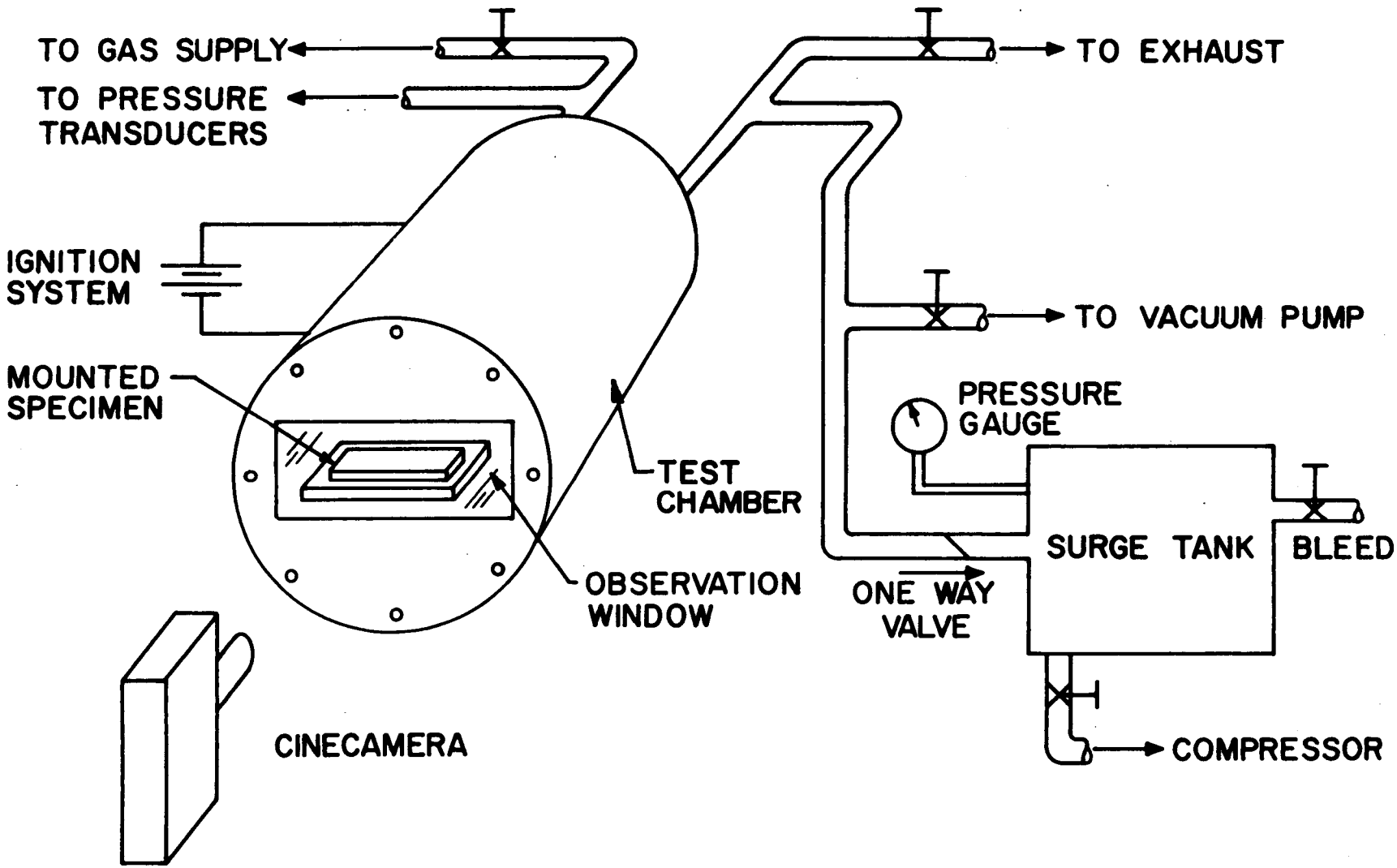

FIG. 1 SCHEMATIC OF APPARATUS FOR FLAME SPREADING VELOCITY MEASURMENT

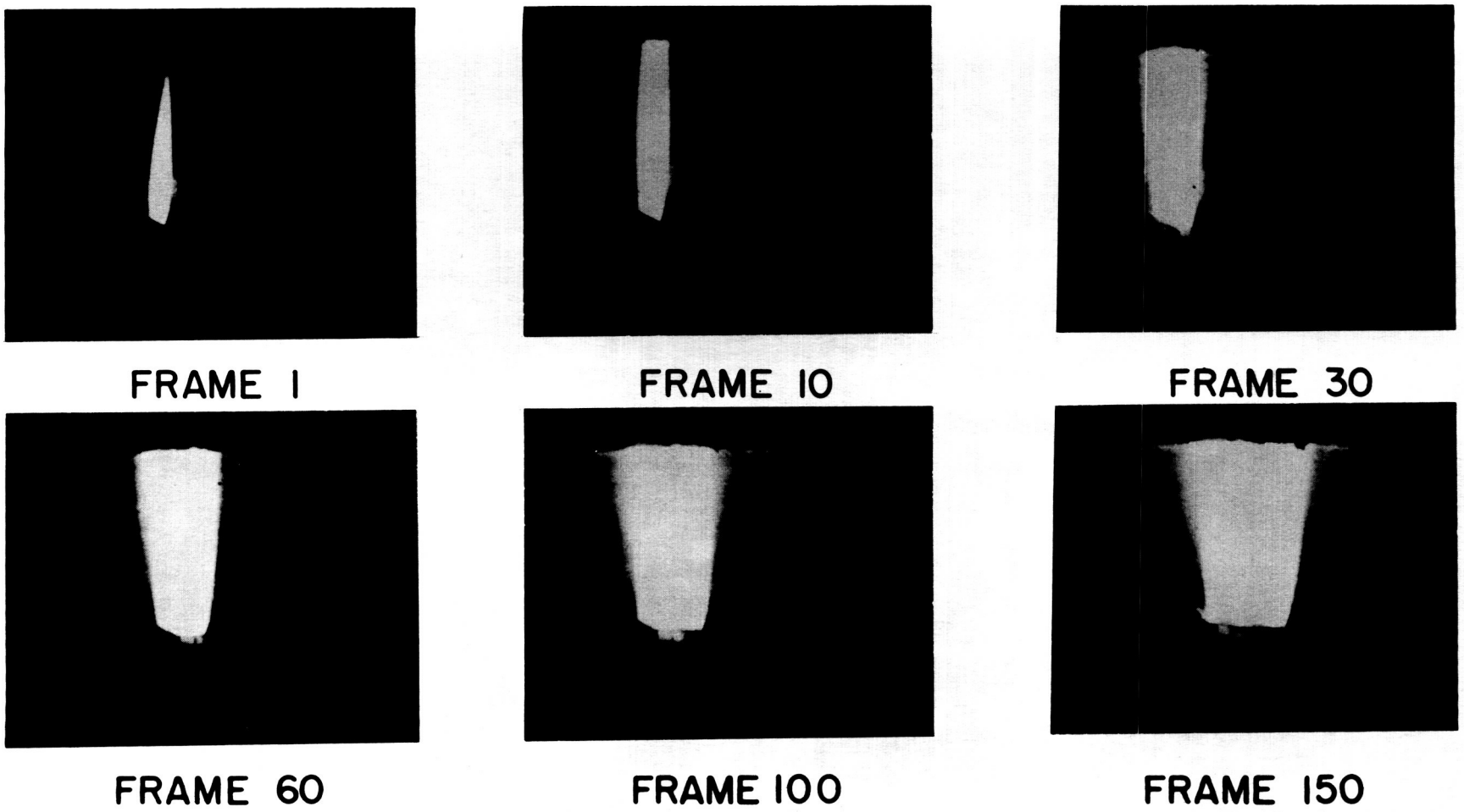

FIG.2 STAGES OF FLAME SPREADING OVER AN IGNITING PROPELLANT SURFACE (48 FRAMES/SEC)

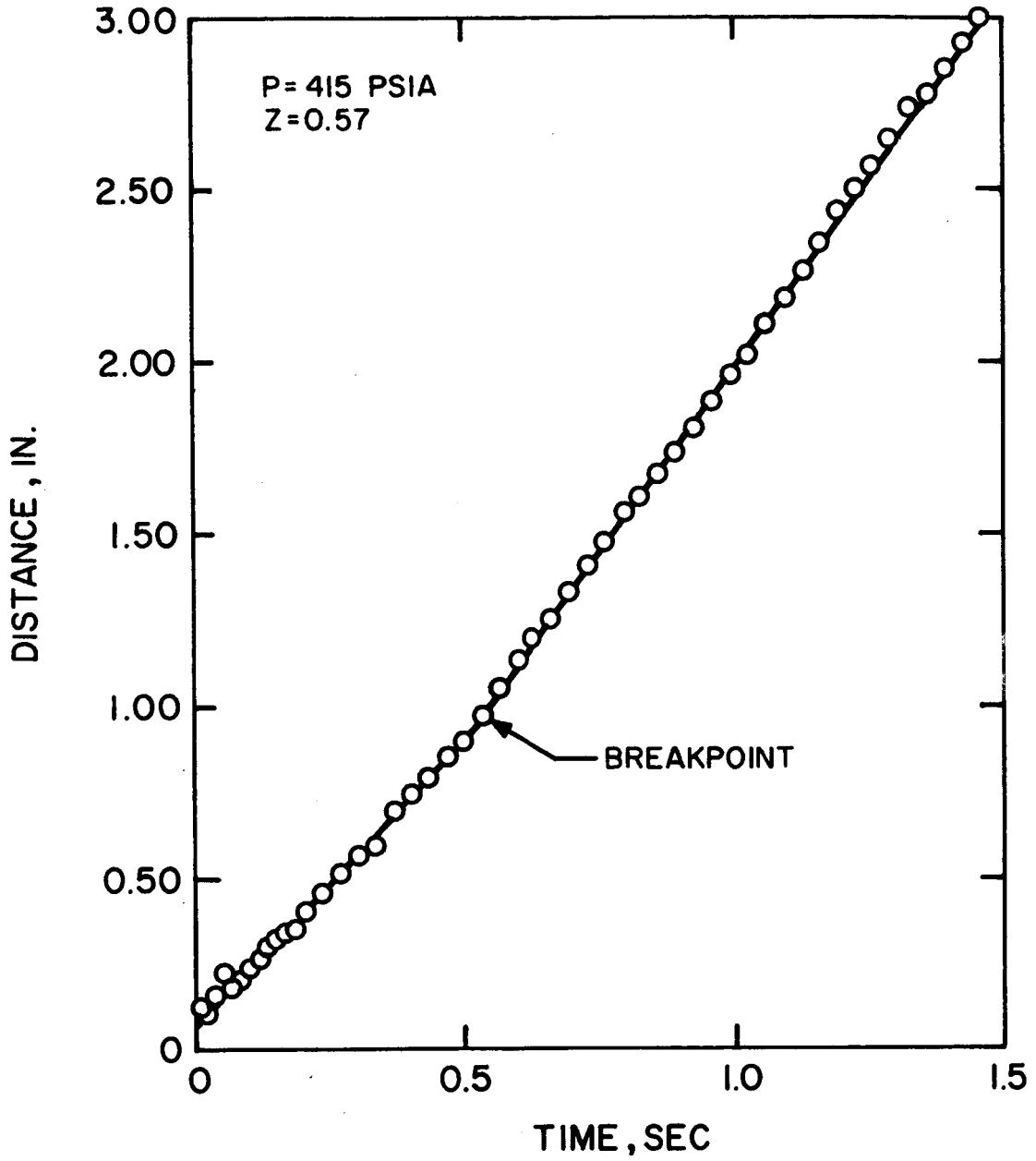

FIG. 3 TYPICAL DISTANCE SPREAD VS TIME FOR PROPELLANT A

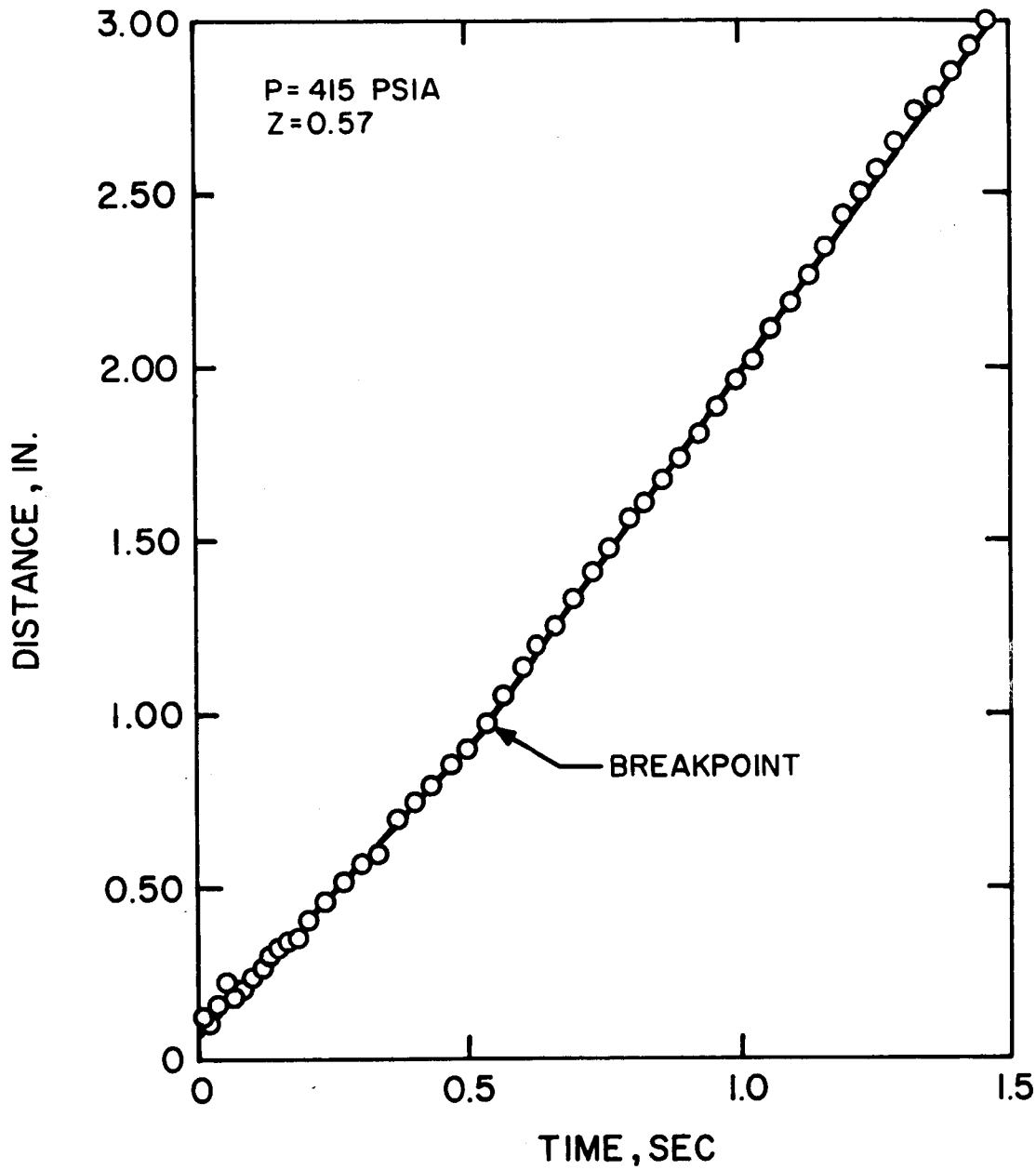

FIG. 3 TYPICAL DISTANCE SPREAD VS TIME FOR PROPELLANT A

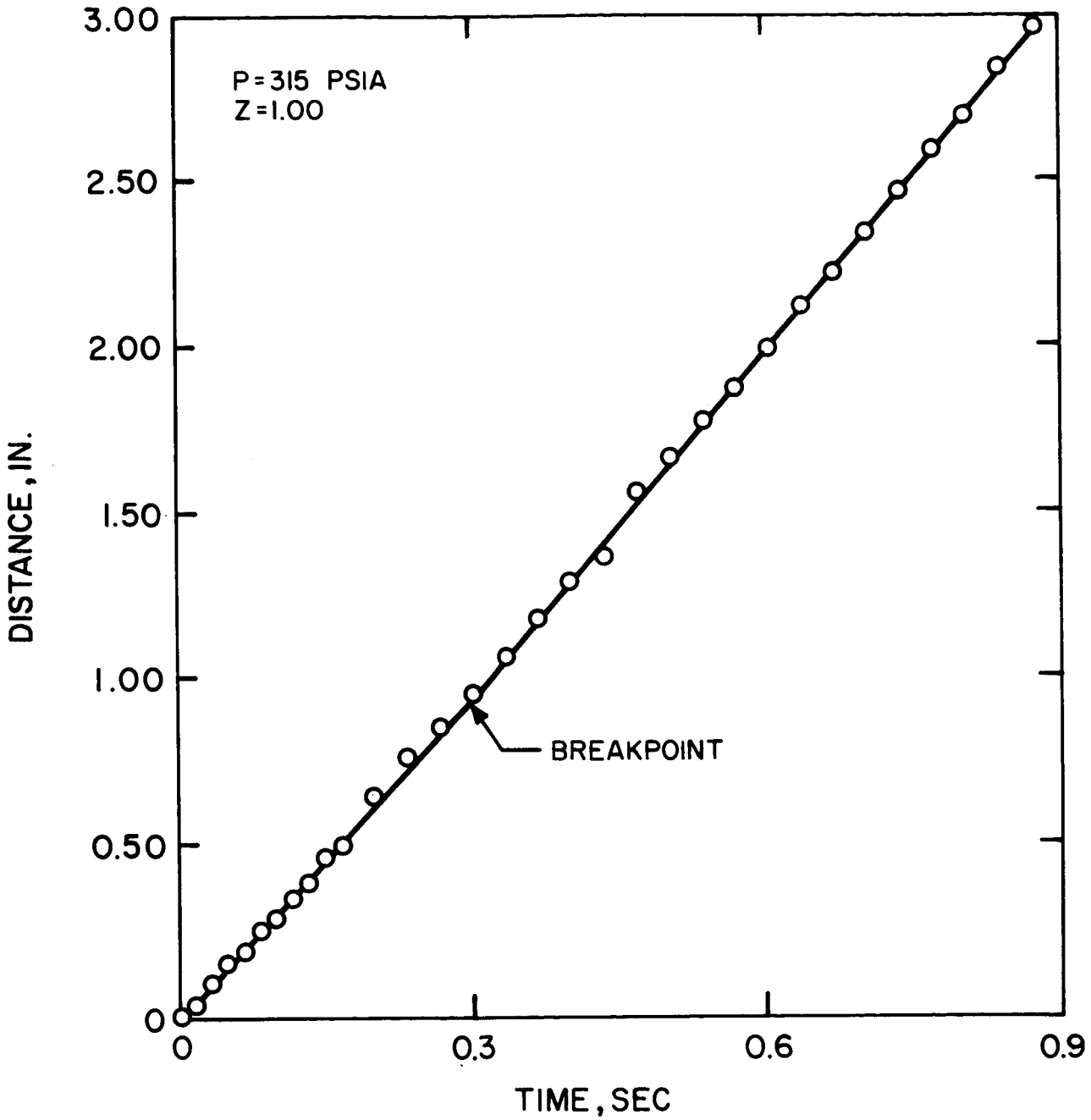

FIG. 4 TYPICAL DISTANCE SPREAD VS TIME FOR PROPELLANT B

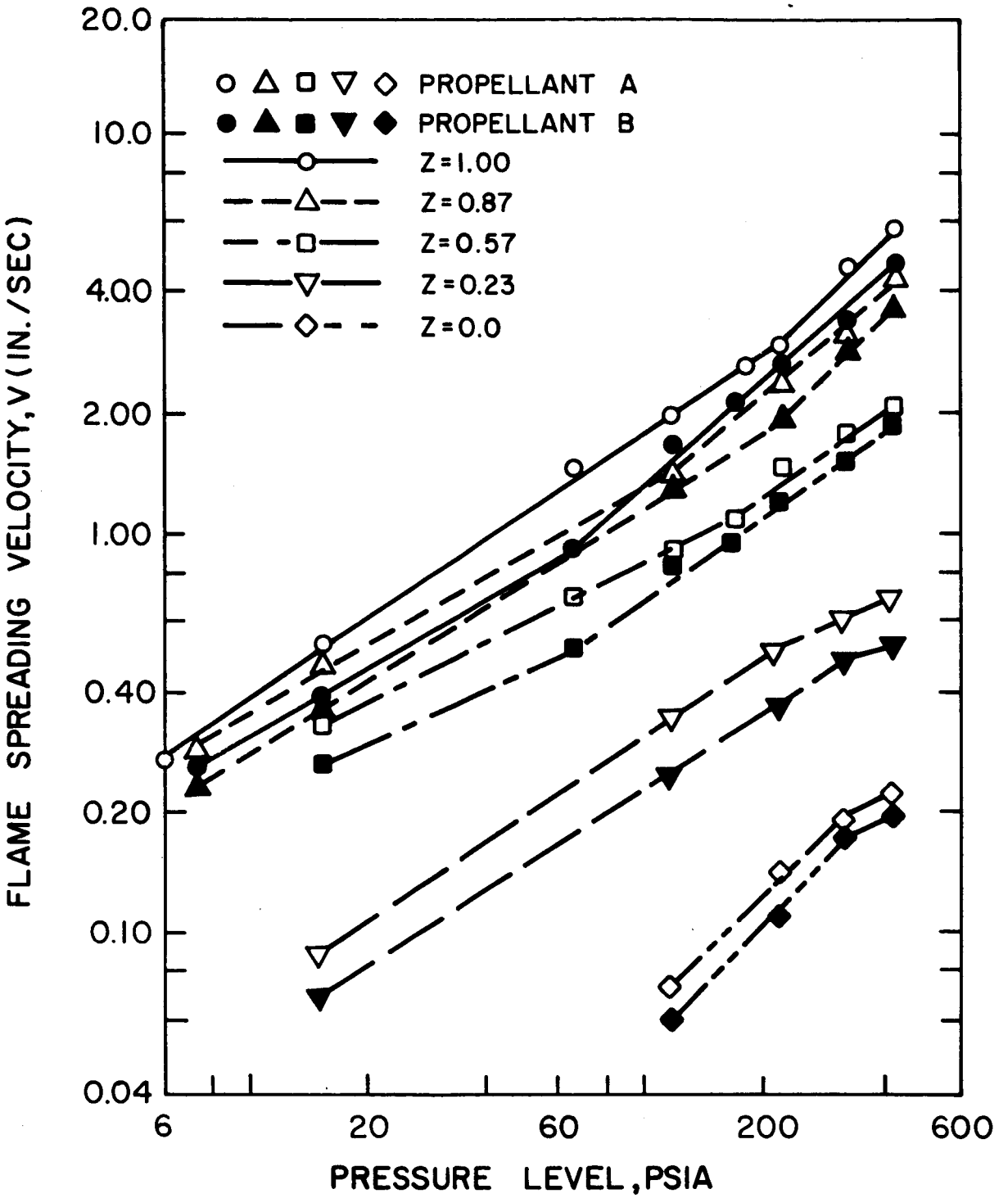

FIG.5 INFLUENCE OF P ON V AT DIFFERENT Z FOR TWO NITRATE ESTER PROPELLANTS

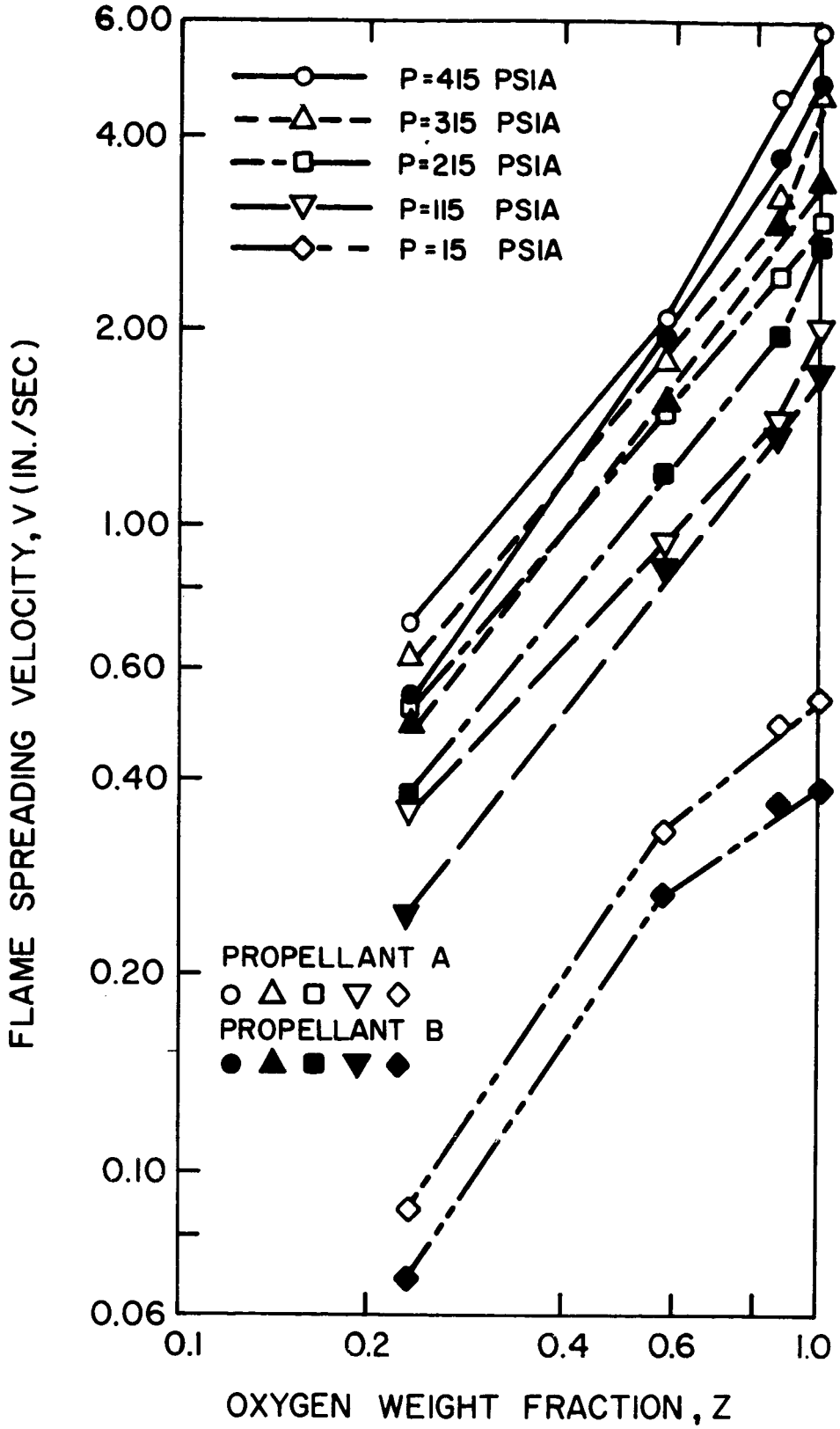

FIG. 6 INFLUENCE OF Z ON V AT DIFFERENT P FOR TWO NITRATE ESTER PROPELLANTS

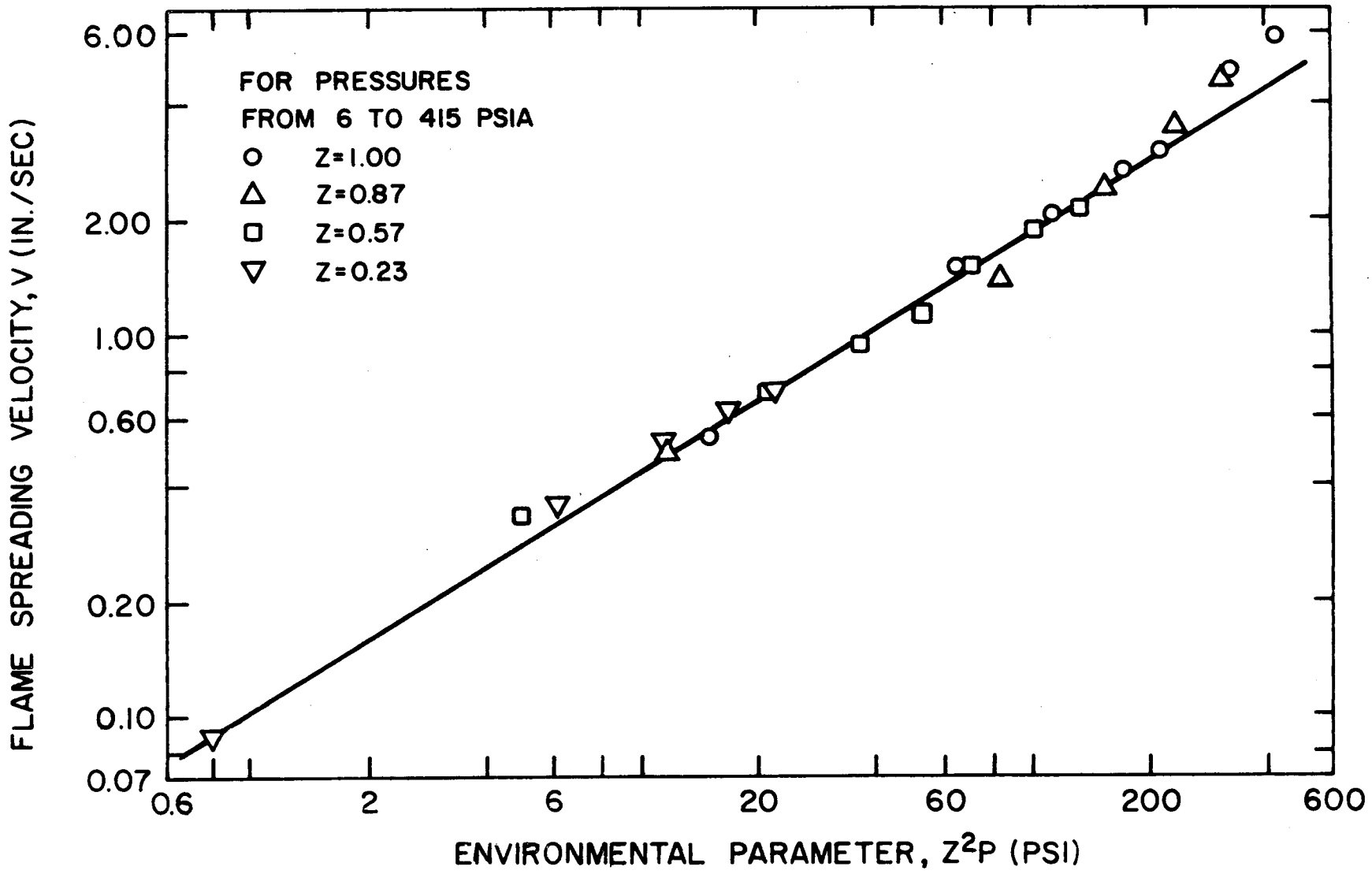

FIG. 7 LOG V VS LOG Z^2P FOR PROPELLANT A

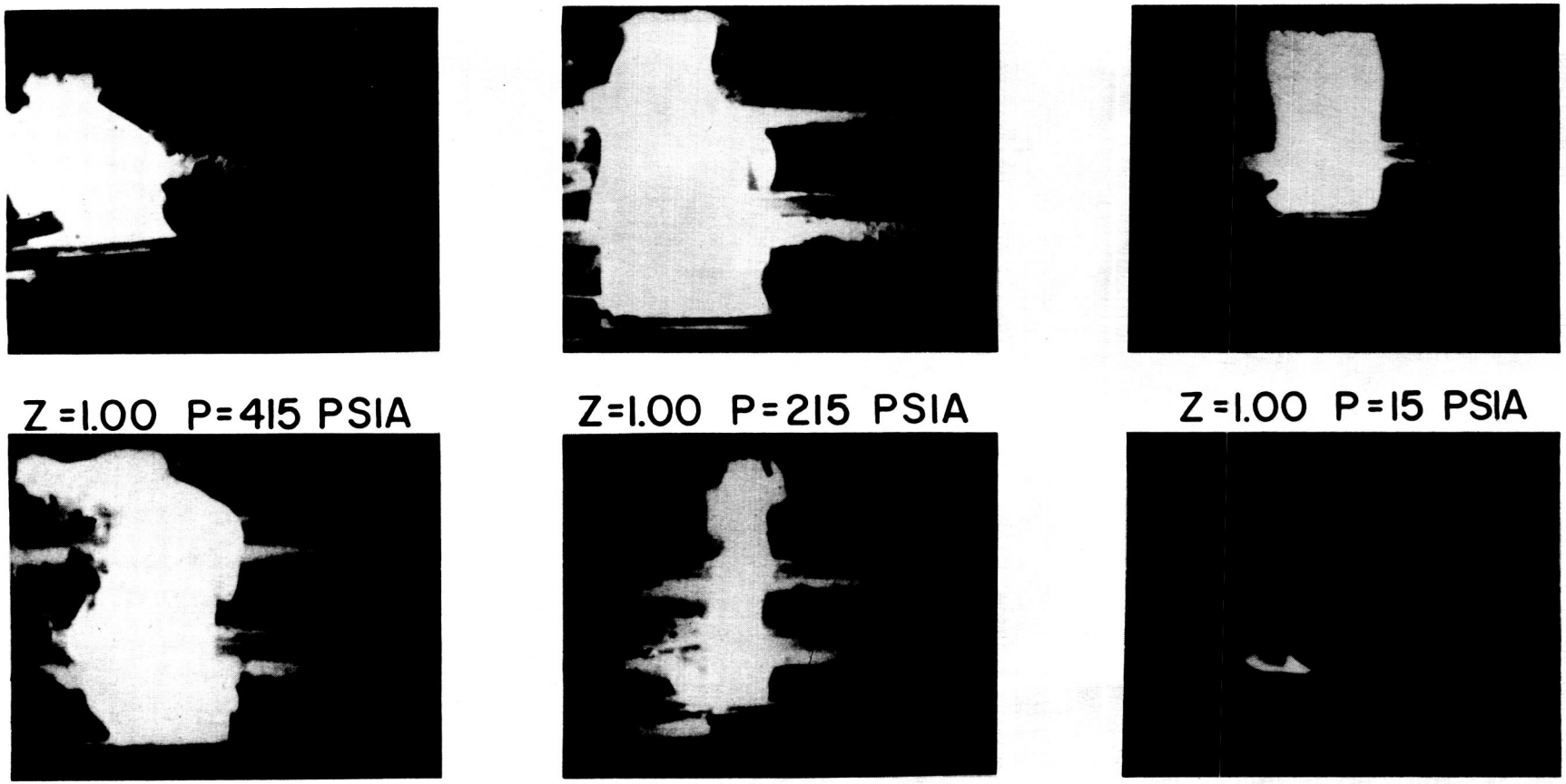

FIG. 9 TYPICAL CHANGES IN FLAME SHAPE AS A FUNCTION OF P AND Z FOR PROPELLANT A